THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INCREASED YIELDS IN ALKALINE PULPING. II. A STUDY OF OPTIMUM CONDITIONS FOR USE OF ADDITIVES IN THE PREVENTION OF PEELING

Project 2942

Report Five

A Progress Report

to

MEMBERS OF GROUP PROJECT 2942

December 21, 1973

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SUMMARY

The stopping reaction was investigated, with cellobiose as a model compound, and the postulated glucosyl-metasaccharinic acid analyzed for with the phenol-sulfuric acid reagent. A certain amount of residual alkali-stable products was formed; it was acidic in nature and a kinetic product, not an impurity in the original cellobiose. In contrast to statements in the literature, calcium base does not increase the yield of this product appreciably over that of the sodium base. There is very little evidence at present that this product is a disaccharide acid possessing a glucosidic bond, and that it is diagnostic of the stopping reaction.

Preliminary reductions of cellobiose (at 45°C) with sodium borohydride have shown a much faster rate in aqueous solution (pH about 10) than in 0.1N sodium hydroxide. Problems have been encountered with evolution of hydrogen in the flow lines of the reactor and possible solutions are discussed.

The oxidation of cellobiose with anthraquinone sulfonic acids has been explored briefly; analyses of the reaction system for unreacted cellobiose are complicated by the presence of the reduced anthraquinone sulfonic acids.

The flow reactor has been modified by using an intermittent operation so that reaction times above 30 seconds can be studied. Thermistors have also been installed in the reaction coils so that the temperature can be monitored continuously along with the movement of liquid in the reaction coils and in the quenching operation. This monitoring of temperature will be valuable in studying reactions with relatively unstable reagents (i.e., sodium borohydride).

INTRODUCTION

The first four reports on this Project dealt with the peeling reaction, a study of the rate of this reaction with cellobiose as a model compound. The rates for peeling in alkali of varying concentrations were studied at temperatures ranging from 30°C up to 170°C, under the conditions of alkaline pulping. The reaction was also studied with kraft pulping white liquor at 150°C.

At these higher temperatures the rates observed were very rapid, so that the reactions observed were completed in a matter of less than a second. To measure these fast reactions a flow reactor was constructed, first a model of glass for lower temperatures, then one of stainless steel to operate at temperatures above 100°C and pressures up to 200 psig. For these fast reactions, with half-lives down to 5 milliseconds, an oscillograph recorder, with chart speeds up to 80 inches a second, was used to record the movements of the syringes driving the liquid through the reaction coil of the flow reactor.

The alkaline reaction solutions, formed by rapidly mixing hot alkali and hot sugar solutions, were quenched, after a given reaction time, by mixing with boric acid solution. These mildly acidic solutions were analyzed by gas chromatography; in this way the rate of disappearance of cellobiose and the appearance of glucose as a product of peeling could be measured. This was the first time that the peeling reaction was shown to occur at higher temperatures. Before this work, the peeling reaction has been studied at temperatures only below 100°C; the rate of disappearance of cellobiose had been measured up to 75°C and the appearance of glucose as a product of peeling had been shown only at room temperature. However, this reaction had been postulated to occur also at higher temperatures and especially with polysaccharides under alkaline pulping conditions. The work on

this project definitely showed that this same peeling reaction occurs at higher temperatures; a regular increase in reaction rate was shown with increase in temperature up to 170°C, and glucose was also shown to be a product at these higher temperatures.

Now in the second phase of this project we are concerned with investigating various ways of stopping or minimizing the peeling reaction, occurring in carbohydrates when treated with alkali at elevated temperatures, in the hope that optimum conditions can be established for producing these same beneficial effects. This program was discussed in detail in our Proposal No. 2068.

In the present report the primary investigation has been that of the "stopping reaction," with cellobiose as a model compound. Alkaline reactions were carried out at 75°C for extended periods of time. It was desired to (a) check the validity of the occurrence of this reaction with cellobiose, and (b) to study the extent of this reaction, relative to peeling, under various conditions of temperature and alkali concentrations.

A few preliminary experiments have been done on the borohydride reduction of cellobiose and also on oxidations with anthraquinone sulfonic acids.

The flow reactor has been modified to allow the study of relatively slow reactions, those taking more than a few seconds. Problems of flow of liquid through the reactor at these slow rates have been studied. The switchboard and oscillograph recorder have been altered, and thermistor sensing units intalled in the reactor coils. These modifications are described in detail.

The oximes of cellobiose and of glucose have been prepared and their trimethylsilyl derivatives run on the gas chromatograph in preparation for study of the reaction system of cellobiose and hydroxylamine in alkali.

The bulk of our efforts during the last six months were in two areas, the stopping reaction and the modification of the flow reactor. The investigation of the stopping reaction will be completed shortly, and the flow reactor will be used to study the borohydride reduction in detail. Experiments will be run under pressure and with minimum heating times to avoid evolution of hydrogen. The use of thermistors will be very helpful in this area.

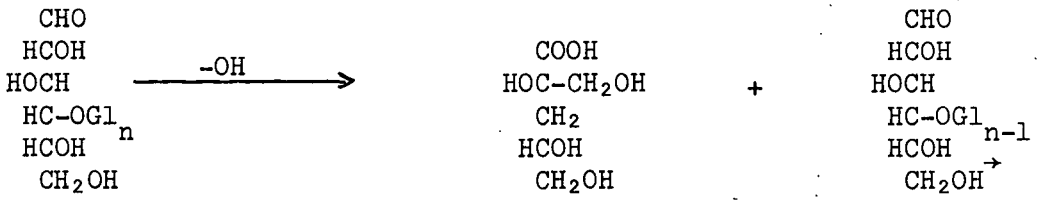
Gas chromatography will be used more in the next phase of our work, with the use of internal standards to give quantitative meaning to the quench solutions obtained from the flow reactor.

With the exception of the stopping reaction, the other investigations have been of an orientation nature only. Ideally, the work on the stopping reaction should have been brought to a close before this report was completed. However, we feel it is important to issue reports to the cooperators on a chronological basis; this serves to keep the cooperators acquainted with the current progress of our work and it serves to give us deadlines to work against. At any time we are willing to answer individual inquiries as to our current progress or to hear comments about the work we have produced.

THE STOPPING REACTION

BACKGROUND

In the alkaline degradation of polysaccharides, or of cellobiose as a model compound, the major reaction is peeling, the breaking of the glycosidic bond adjacent to the end group. This end group, with a free carbonyl group, facilitates the elimination of the glucosyl unit at C-4. The two products are a shorter polysaccharide chain (or glucose in the case of cellobiose) and a C_6-acid, called isosaccharinic acid (Fig. 1). The new polysaccharide can peel again to form a shorter chain, with n-2 units. This peeling reaction, which is very fast, can be repeated indefinitely as long as a unit with a free carbonyl group is formed on the new n-x polysaccharide.



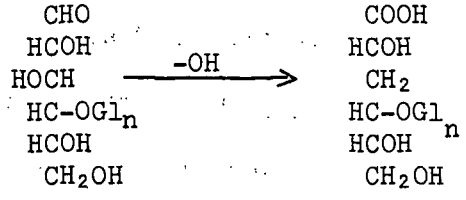
α-Isosaccharinic Acid

Figure 1. Alkaline Degradation of Polysaccharide with Peeling (for Cellobiose, n = 1)

However, there is a much slower reaction, occurring simultaneously with the peeling reaction; this stopping reaction involves the elimination of the OH group at C-3 of the end unit, instead of the glucosyl group at C-4, and results in a glucosyl-metasaccharinic acid (GMS) end unit (Fig. 2). This reaction, the formation of an acidic end unit, has two valuable features.

(1) The glucosidic bond is not broken during the formation of the GMS unit.

(2) The glucosidic bond of the GMS unit is resistant to alkaline degradation so that no peeling can occur.



Glucosyl-metassaccharinic Acid (GMS)

Figure 2. Alkaline Degradation of Polysaccharide with Stopping (for Cellobiose, $n = 1$)

Unfortunately this stopping reaction, while fast, is much slower (by the order of 50 times or more) than the peeling reaction; there is much less tendency for the OH group at C-3 to be eliminated than for the glucosyl group at C-4. In this type of alkaline elimination the glucosyl group is referred to as a good leaving group, and the OH group as a poor leaving group. However, it has been claimed that variation of alkaline conditions, such as use of calcium instead of sodium based systems, tend to increase the extent of the stopping reaction (1), and our present work is involved with study of such variation of conditions.

The stopping reaction was originally investigated on polysaccharides by Samuelson and coworkers (2), and also by Richards and coworkers (3). The former found that about 50 glucose units were peeled before an alkali-resistant linkage was formed. The latter group of workers hydrolyzed an alkali-stable polysaccharide possessing an acidic end unit formed by the stopping reaction; the mixture of glucose and a small amount of acid was carefully fractionated and the acid identified as glucometasaccharinic acid. This last work demonstrated that the acidic end unit was formed by alkaline rearrangement and not by oxidation.

Lindberg, et al. (1) investigated the stopping reaction with various disaccharides as model compounds. These were treated with alkali until the reaction was driven "to completion"; a small amount of an alkali-stable product with a glycosidic bond was found. The analysis for the glycosidic bond was done by measuring the color produced by a phenol-sulfuric acid reagent at 490 nm (4). It was assumed that the reagent hydrolyzed the bond and the color was then formed from the liberated sugar; this was verified in the case of cellobiose by hydrolyzing a sample separately with 2N sulfuric acid and then determining the liberated glucose by gas chromatography.

These Swedish workers found the yield of alkali-resistant material derived from cellobiose and 0.02N sodium hydroxide decreased with increasing temperature (60 to 90°) and extrapolation to 170°C gave them a value of 2%, agreeing with the data of Samuelson (2). They also isolated a small amount of a sirupy acid by column chromatography, which on hydrolysis gave glucose and metasaccharinic acid.

Other workers (5) have been unable to confirm the isolation of the glucosyl-metasaccharinic acid, and have concluded that cellobiose, as a model compound, does not undergo a stopping reaction, in contrast to cellulose.

We have repeated the work of Lindberg, et al. (1), especially the alkaline degradation of cellobiose, and monitored our reactions with the phenol-sulfuric acid reagent (PSA). We were hopeful that this PSA test would be a valid test for studying the stopping reaction, and that we could determine optimum conditions, in regard to relative rates of peeling and stopping, for the initial stages of alkaline pulping reactions. Our results agree only in part with that of the Swedish workers and at present we are not certain that the "residual absorbance" obtained with the PSA method is diagnostic of a glucosyl-metasaccharinic acid, and can be used to study the stopping reaction.

DISCUSSION OF EXPERIMENTAL RESULTS

The alkaline degradation of cellobiose was carried out at 75°C to completion and the remaining glycosidic bonds analyzed by the phenol-sulfuric acid (PSA) method. We have run these degradations for times from 5 to 72 hours to check "completeness of reactions"; the Swedish workers (1) do not specify their reaction times. We do get a certain amount of residual absorbance, as shown in Fig. 3. This amount is about 3.2% at the most, if the absorbance is translated into units of cellobiose. The several solutions, calcium and sodium hydroxide, seem to end at almost the same values, 3.2 and 2.7%, respectively. We do not get the great differences reported earlier (1), values of 10.8% and 3.4%, for the two types of bases.

The only effect we can see in varying the nature of the base and concentration is upon the rate of reaching the level of residual absorbance, i.e., completion of peeling (removal of all cellobiose and glucose). These changes do not seem to affect greatly the yield of alkali-resistant GMS, the only compound that is left presumably, that will react with the PSA reagent.

We have investigated the nature of this "GMS" in solution, using the various solutions with residual absorbances, and have obtained the following information. In this investigation the solutions were monitored by the PSA reagent; "it" below refers to a compound reacting with this reagent.

(1) It is acidic in nature; it is absorbed from alkaline or acidic solutions by a mixed-bed (MB-3) resin, and is removed again from this resin by alkaline elution.

(2) It is not reduced by sodium borohydride, showing the presence of a protected glycosidic bond. Similar reductions of mixtures of glucose and

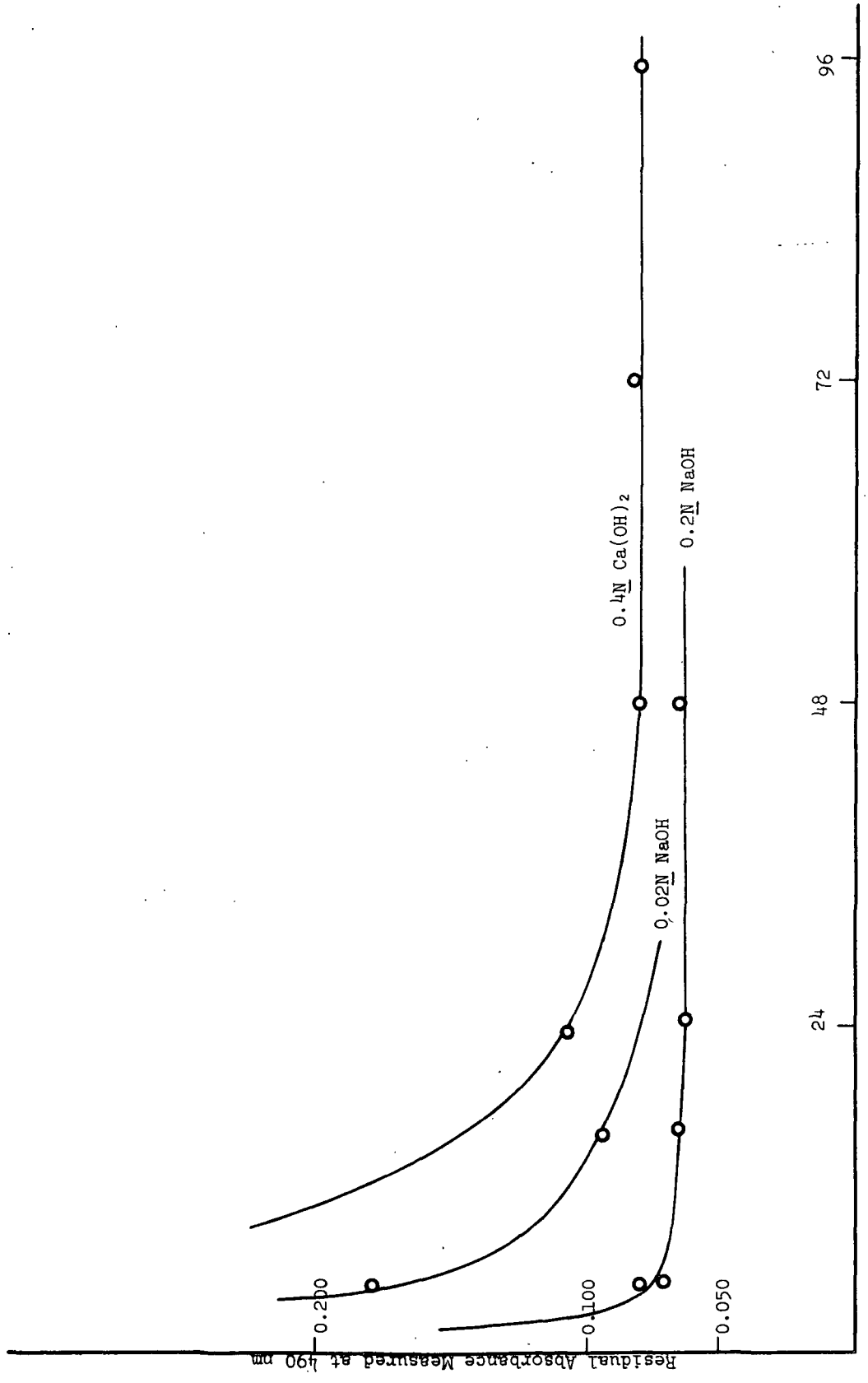


Figure 3. Residual Absorbance Obtained with Cellobiose in Alkaline Solutions

cellobiose will show a lessening of this PSA color. Thus (Fig. 4), solutions that had been treated with lime for 48 hours apparently still contained glucose or cellobiose; this was shown by the effect of borohydride reduction. At 72 hours the absorbance was not affected by borohydride reduction.

(3) The color formed from the GMS in the PSA reaction shows a maximum at 490 nm, similar to that obtained from glucose or cellobiose. So this color, obtained from the residual alkali-resistant material, can be considered diagnostic of a glucosidic bond.

(4) The compound is a kinetic product and not an impurity in the original cellobiose. This was shown by running alkaline degradations for short periods of time with 0.2N sodium hydroxide, and then analyzing the reaction system for yields of GMS. The yields obtained were roughly proportional to the extent of reaction (Fig. 5). The separation of the GMS from the unreacted cellobiose and glucose in the system, before PSA analysis, is described later in this report. The separation is a sort of "needle in a haystack" procedure, and a large blank value was found for the zero reaction.

In Table I is listed the behavior of glucose, cellobiose and GMS with the PSA reagent under various conditions. It is assumed here, based on data cited in the literature (1), that the saccharinic acids, of C_6 and smaller size, do not contribute to the PSA color.

The above four points are all positive, in favor of the existence of a stopping reaction, monitored by the PSA reaction. However, there are several adverse experiments, which may refute the existence of such a reaction, at least of the magnitude shown above (yields of several percent of GMS). These should be checked out to established whether GMS really exists or whether the residual absorbance is due to an artifact.

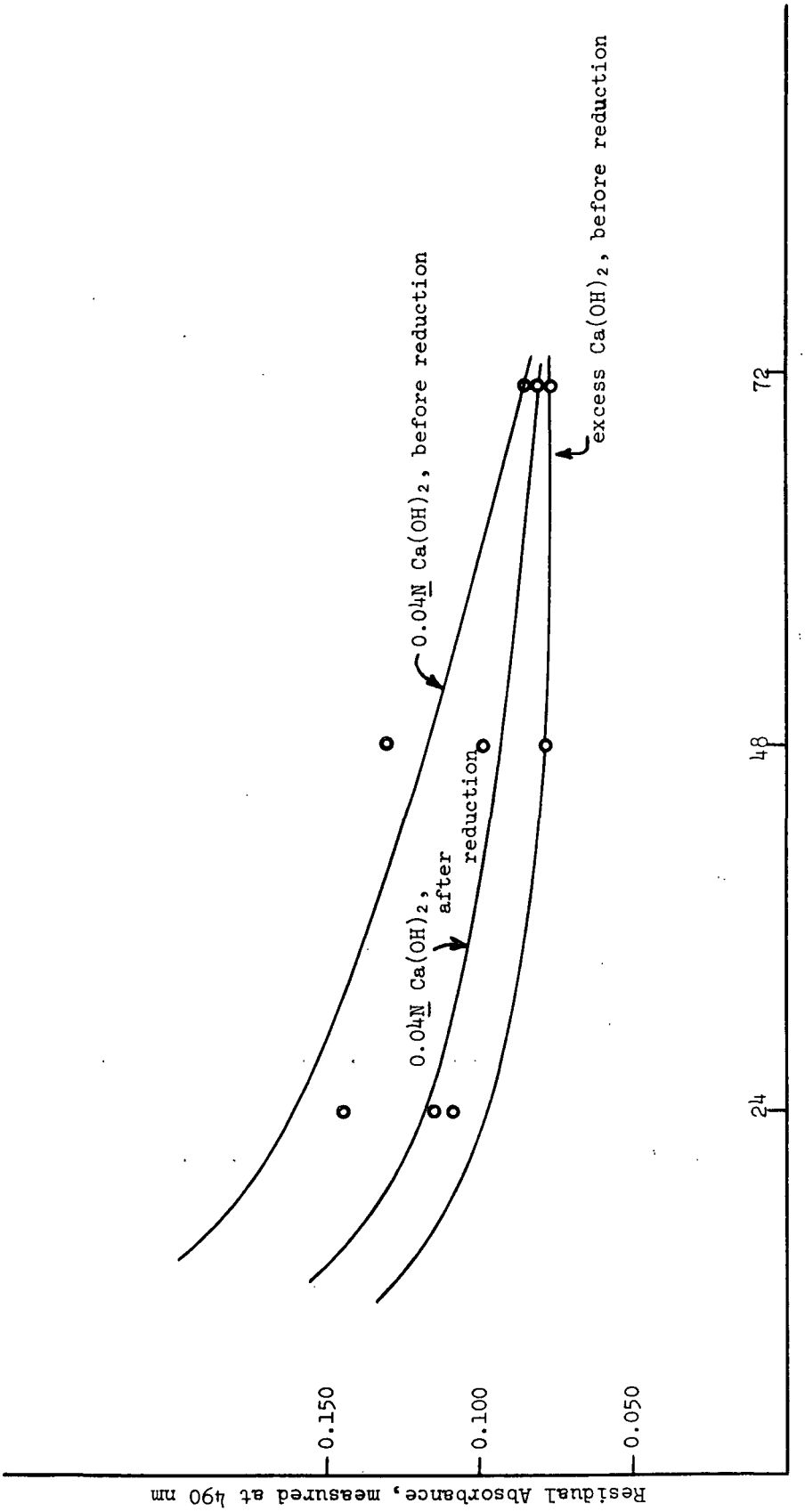


Figure 4. Residual Absorbance for Cellobiose Treated with $Ca(OH)_2$ at 75°C

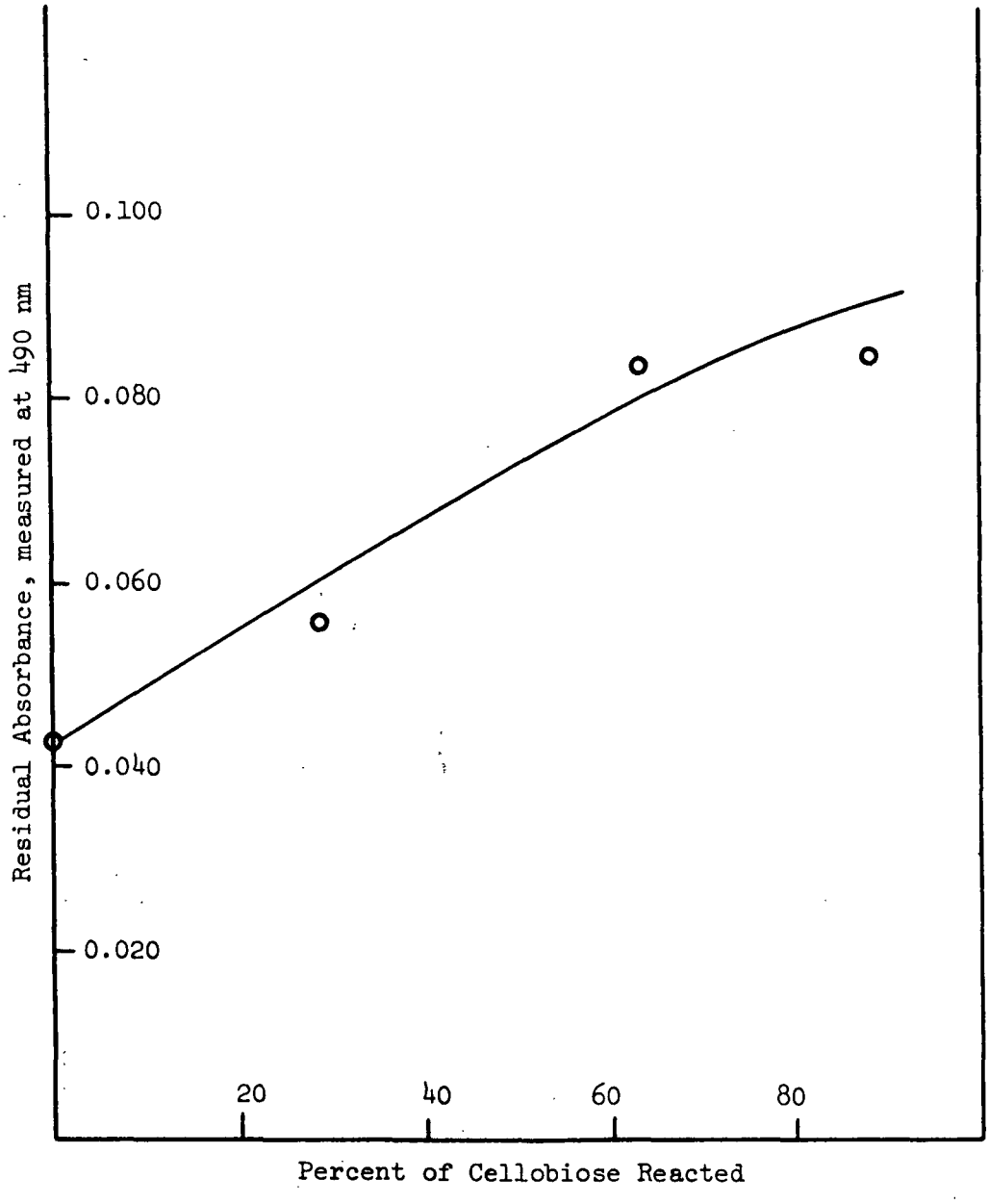


Figure 5. Increase of Residual Absorbance with Extent of Reaction

TABLE I

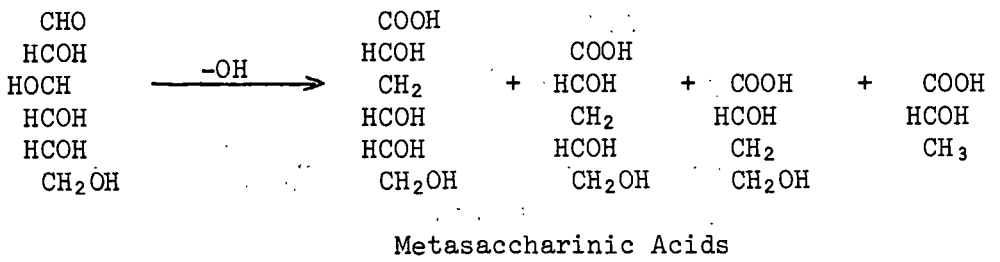
BEHAVIOR OF VARIOUS COMPOUNDS WITH PSA REAGENT

System Studied	Color Developed for Glucose	Cellobiose	Glucosyl-metasaccharinic Acid (GMS)
Aqueous solution	+	+	+
Alkaline solution	less	less	+
Extreme treatment with alkali (2-3 days, 75°C)	--	--	+
Aqueous solution, after borohydride reduction	--	+	+
Same, after treatment with MB-3 resin	--	+	--
Alkaline effluent from MB-3 resin	--	--	+

Note — the color is measured at 490 nm, after development with the phenol-sulfuric acid reagent.

(5) We have not been able to isolate the GMS as a separate product by gas chromatography. Such analysis, after trimethylsilylation of the reaction mixtures, show strong peaks for isosaccharinic acid, and many small peaks for the various metasaccharinic acids formed from glucose (Fig. 6)*. Several slower peaks, toward the disaccharide region, were noted. However, these peaks did not disappear after acid hydrolysis; such disappearance would be expected if a peak were GMS.

*In the case of glucose, the OH group at C-3 is eliminated, rather than that at C-4, due to its closer distance to the activating carbonyl group at C-1. Also there is fragmentation of the hexose originally, so that the acids formed range from C_6 to C_3 in composition.



Metasaccharinic Acids

Figure 6. Alkaline Isomerization of Glucose to Metasaccharinic Acids

(6) The residual absorbance may be derived from an artifact from glucose or from cellobiose. For a solution containing primarily glucose or cellobiose, the PSA absorbance is proportional to the concentrations of these sugars. However, as these sugars are destroyed, the absorbance from the PSA test will decrease, but we have no evidence that rules out the formation of non-sugar compounds that will react with the PSA reagent. Thus, Garrett and Young (6) showed the formation of unknown compounds in alkaline solutions of glucose that absorbed in the ultraviolet at 270 and 310 nm. These chromophores might react with the PSA reagent to give a color that could be confused with that from a glycosidic bond.

To check this, we will run alkaline reactions with glucose alone, and find out if any residual absorbance is observed. There is little possibility of a glucosidic bond here; any absorbance observed after the glucose is destroyed must be due to an artifact. Such absorbance will be checked for possible acidic nature.

(7) The hydrolyzate from an alkaline residual solution of cellobiose will be analyzed by gas chromatography for the presence of glucose. Lindberg, et al. (1) claimed to have found this sugar by hydrolysis of an alkaline solution, carried "to completion," and claimed the amount of sugar found by gas chromatography checked with that found by the PSA method. We will reduce the hydrolyzate, remove

acidic material with a mixed-bed resin, and then look for a glucitol peak on the gas chromatograph of the neutral effluent.

(8) In (3) above, it was mentioned that a color maximum for the residual absorbance was observed at 490 nm. similar to that obtained from glucose and cellobiose. To check this, we will run detailed absorption curves for the color derived from (a) glucose, (b) cellobiose, and from alkaline solutions of glucose, (c) and of cellobiose, (d) carried to completion. If (c) and (d) are different from (a) and (b), we can conclude that the latter colors are due to artifacts.

The above experiments (6 to 8) will be investigated briefly, again at 75°C. If they refute the presence of GMS, we will not pursue the stopping reaction with cellobiose any further, except for possibly one or two experiments at 120°C. We had high hopes initially that we could obtain valuable rate data on this reaction by use of cellobiose as a model compound, and with the PSA method as a diagnostic tool. At present we have misgivings about this approach, and will abandon it if we find it is not feasible.

EXPERIMENTAL DETAILS FOR THE STOPPING REACTION

ALKALINE DEGRADATIONS

Solutions of 25 mg cellobiose in 25 ml aqueous alkali were prepared under nitrogen. The alkali was first boiled to remove air, cooled, then added to the cellobiose in a round bottom flask. The latter was sealed with a ground joint attached to a stopcock. The system was then alternately evacuated and filled with nitrogen five times.

The flask, containing the solution under nitrogen, was then placed in an oil bath at 75°C for a given period of time, removed and cooled.

The solutions were either analyzed directly by the PSA method (1-ml aliquots taken) or reduced first with sodium borohydride. In the latter case the solutions were then subjected to removal of borate, etc. (see Progress Report One, page 8) and concentrated to dryness. The dry residue was then dissolved in 25 ml of water (added with a pipet) to give the original volume again. One-ml aliquots of this solution were taken for the PSA method.

The two methods gave similar results, where the alkaline solutions had been carried out for long periods of time, i.e., where no cellobiose or glucose remained in solution. For reactions of shorter duration, the borohydride reduction was always used.

PHENOL-SULFURIC ACID DETERMINATION

This was the heat-of-dilution method (4), run on one ml of reaction solution, where the latter contained 100 µg of cellobiose or less. This method gives linear absorbance values up to 0.300 at 490 nm. Since we do not know the

absorbance value for GMS, the data reported are expressed in cellobiitol equivalents, i.e., where only a glycosidic linkage is involved.

Where absorbances were very weak, residual solutions were often concentrated to give a value appreciably greater than the blank, and corrections made for the change in concentration.

In all cases absorbances reported are based on a solution containing originally a concentration of 1 mg cellobiose/ml (see Table II).

SEPARATION OF ACIDIC PRODUCTS FROM NEUTRAL CARBOHYDRATES

Partially reacted solutions, containing cellobiose and glucose, as well as various saccharinic acids, were first reduced with sodium borohydride. This was done at a pH of 10 or above. The sugars were converted to the alditols (cellobiitol and glucitol) and the saccharinic acids present were not reduced, being in the salt form. Care was taken to keep the pH at 10 or above, to prevent lactone formation; lactones can be reduced by borohydride and will give new reducing sugars. These latter compounds might react in the PSA method.

The reductions were allowed to continue overnight (5 mg sodium borohydride per ml of solution), and then the system was treated with IR-120 resin and methanol to remove borate. The dry residue was then dissolved in 25 ml water to give the original concentration again.

One-ml aliquots were taken for the PSA method; in some cases dilution was necessary to keep the sugar alcohols in the 100 μg range.

The bulk of the solution was passed slowly through a column containing 20 ml of MB-3 mixed bed resin. The resin was then washed slowly (1000 ml water in

2 hours) to remove the neutral components (cellobiitol and glucitol). The saccharinic acids and lactones were mostly retained on the resin; this was confirmed by gas chromatography.

TABLE II

ANALYSES OF ALKALINE SOLUTIONS OF CELLOBIOSE

Base Used	Time Reaction hr at 75°C	Absorbance, from PSA method
0.02N NaOH	5	0.177
	16	0.093
0.2N NaOH	5	0.070
	16	0.064
	5	0.079
	24	0.061
	48	0.065
0.04N $Ca(OH)_2$	24	0.143
	48	0.131
	72	0.082
Same samples but reduced with borohydride	24	0.113
	48	0.098
	72	0.083
0.04N $Ca(OH)_2$ and excess solid $Ca(OH)_2$	24	0.107
	72	0.078
	72	0.077
0.2N NaOH	0	4.400
	10 minutes	3.175
	15 minutes	1.630
	20 minutes	0.540
Same samples, absorbed on MB-3 resin and eluted with 1N NaOH		
	0	0.043
	10 minutes	0.055
	15 minutes	0.083
	20 minutes	0.084

Note — all data are for samples based on a concentration of 1 mg/ml of cellobiose originally. Absorbance values above 0.200 are calculated from diluted samples of lower absorbance.

After the resin had been washed with water, it was treated with 30 ml of 1N sodium hydroxide and then 120 ml water. The alkaline effluent was treated with IR-120 resin to remove sodium ions, and then concentrated to dryness.

The residue, containing mostly saccharinic acids, and hopefully very little cellobiitol and glucitol, was dissolved in 25 ml water, and this solution analyzed by the PSA method. Where the absorbance was low, a solution was made up with only 10 ml water and the resulting absorbance corrected to a 25-ml volume.

It was found that some cellobiitol was retained on the MB-3 resin, despite extensive washing, and so a blank factor, found at zero time reaction, was used (see Fig. 5). An excess of resin is used to retain the saccharinic acids, but some neutrals are absorbed and prove difficult to wash out completely. The blank, at zero time, was shown by GLC to be cellobiitol.

GAS CHROMATOGRAPHY

The various alkaline liquors were investigated qualitatively by chromatography of the trimethylsilyl derivatives. It was found best to trimethylsilylate the saccharinic acids as the sodium salts; in this way only one peak was obtained for each acid. Use of the free acids instead gave a mixture of peaks for lactone and acid.

Analyses were done on an OV-17 column, 1/8 inch x 6 feet, programmed from 100°C to 230°C at 4°/min. Retention times were about 18 minutes and 34 minutes for α-isosaccharinic acid and for cellobiitol, respectively. A large number of smaller peaks, from metasaccharinic acids, had retention times of less than 18 minutes. The GMS peak was looked for in the 30-minute region.

Trimethylsilylation of the sodium salts was best done with a two-phase reagent, a mixture of Tri-Sil Concentrate (7) and dimethyl sulfoxide. The trimethylsilyl derivatives dissolve in the upper layer, and the by-products in the lower dimethyl sulfoxide layer. Neutral compounds, such as cellobiitol or cellobiose, were trimethylsilylated with Tri-Sil (7) or Tri-Sil-Z (7); these are one-phase reagents. The sodium salts of the acids could also be trimethylsilylated with Tri-Sil, but the reaction is much slower.

Generally, it was found that 1 mg of sample, trimethylsilylated with 500 µl of reagent, was sufficient for adequate peaks on the chromatograph (2-µl injections). The usual procedure was to prepare a borate-free solution of the sample, in a concentration of about 1 mg/ml and pipet one ml into a 6-ml glass Hypo-Vial (7). This solution was dried down over P_2O_5 in a vacuum desiccator; this usually took overnight. Care was taken that the pressure was not too low (above 25-inch vacuum) to avoid bumping.

The reagent was then added to the dried residue, the bottle sealed with a teflon-lined septum and an aluminum cap (crimped on), and shaken overnight at room temperature. In the case of one-phase reagents, 2-µl samples were removed by syringe via the septum and injected directly on the chromatograph. In the case of two-phase reagents, the mixture was transferred with a 500-µl syringe into a smaller vial, (which was also sealed with a teflon-lined septum (Reacti-Vial, 1-ml size) (7). A 2-µl portion was taken from the upper layer and injected in the chromatograph.

The use of bottles sealed with septums was found to be valuable for keeping the moist atmosphere from the trimethylsilylation mixture. Also, the crimped bottles could be shaken vigorously without leakage. All septums must have

teflon-liners; rubber septums react with the trimethylsilylation reagents and give spurious peaks on the chromatograph.

Aqueous solutions concentrate readily in the larger area of the 6-ml vial, in contrast to the smaller 1-ml Reacti-Vial. The solutions of the sodium salts of the acids were adjusted to pH 10 or 11 before concentration; care was taken to keep the pH high to avoid formation of free acids and possible lactone formation.

REDUCTION OF CELLOBIOSE WITH SODIUM BOROHYDRIDE

KINETICS OF THE REACTION

Two runs were made with cellobiose and sodium borohydride; one was made in 0.1N sodium hydroxide and the other in water solution. The temperature was 45°C for both reactions. The kinetic data gave first-order plots, and the reaction was much faster in the aqueous solution. The half-lives for the water system (pH about 10) and the 0.1N sodium hydroxide system were 1 and 8 minutes, respectively (Fig. 7).

The slower reaction at higher pH is attributed to the possible formation of a cellobiose anion, a negatively charged species which would react slowly with the borohydride anion. While the more alkaline reaction is slower, the stability of borohydride is higher at the higher pH.

Head (8) has pointed out the slower reduction of polysaccharides at higher pH values, and also the slower reduction in a buffer solution of the same pH as that of the aqueous borohydride solution he used. However, his buffer solution contained borate, and perhaps a buffer of another composition might not show this effect.

The kinetic run in 0.1N sodium hydroxide was run in the flow reactor. The other kinetic run was made in glass vessels immersed in the oil bath; aqueous solutions of borohydride tend to decompose rather rapidly, and the hydrogen evolved disrupts the flow system in the reactor. This is discussed more in the next section.

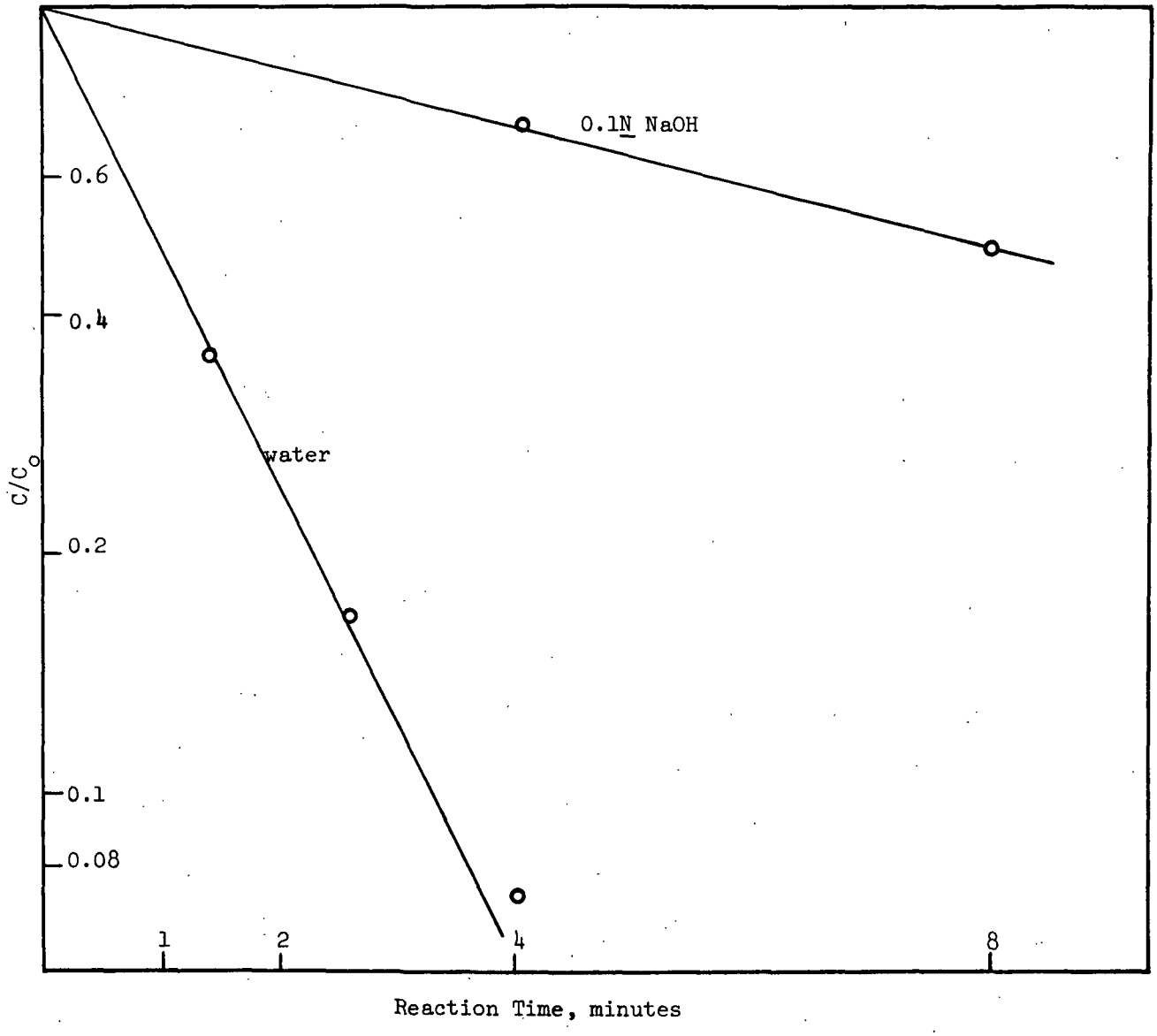


Figure 7. Borohydride Reduction of Cellobiose
First Order Plot

HANDLING BOROHYDRIDE SOLUTIONS IN THE FLOW REACTOR

It was found that dilute sulfuric acid was an effective quenching agent for a borohydride system; the quenched system contained no borohydride. However, use of milder acids, such as boric acid, was not so effective, and about 15% of the original borohydride was still present in the quenched system. The action of such mild acids is rather slow and the final pH is high, about 7, due to buffering. In contrast, the final pH of the systems quenched with sulfuric acid is about 2.

Sodium borohydride solutions decompose very slowly, with the evolution of hydrogen gas. Formation of such gas bubbles in flow lines in the reactor tend to push liquid prematurely in and out of reaction coils. Such pushing action was very slight for alkaline borohydride solutions (in 0.1N sodium hydroxide) but more appreciable in 0.01N sodium hydroxide. These reactions were run at room temperature, and the effects are more pronounced at higher temperatures.

It may be possible to prevent such adverse effects by operating the reactor under nitrogen pressure, in an attempt to counterbalance the pressure created by the hydrogen. Also, with thermistor sensing elements in the reaction coils, it may be possible to operate the flow reactor as rapidly as possible, without waiting for thermal equilibration in the heating coils, and noting the rise in temperature between the two ends of the reaction coil; an average temperature for the reaction can then be calculated.

This is a matter of a time factor — the longer the borohydride solutions remain in the lines, the more gas will be evolved, thus disrupting the flow pattern. With thermistors now connected to the oscillograph the following changes can be made in flow reactor operation.

1. A minimum of "equilibration time" in the heating coils can be maintained. In the past a time of five to six minutes was allowed for this equilibration, after the immersion of the coils filled with the desired liquids. Now the empty coils can be immersed first, allowed to come to temperature, then the liquid added. In this way, observed with the thermistors, a much shorter heating time for liquids can be used.

2. If this minimum time is not satisfactory, the borohydride solution can be run more rapidly through the heating coil, and the temperatures of the solution entering and leaving the reaction coil observed. An average temperature for the dwell time in the reaction coil can be calculated.

3. For a more rapid heat transfer, only the sugar solution can be heated in a heating coil, and the borohydride solution kept in a coil outside the oil bath at room temperature. Then the hot sugar solution and cold borohydride solution will be mixed before entering the reaction coil. The resulting temperature of this mixture will then be used.

4. A combination of the above schemes with applied pressure to combat that created by the evolved hydrogen will also be tried.

ANALYSIS FOR CELLOBIOSE

The method of Willstatter and Schudel (9) consists of the oxidation of the sugar with a known excess of sodium hypoiodite at pH 11, and back titration of the reagent with thiosulfate. In the present work 10 ml of 0.035N potassium iodate is added to the sugar solution (5 to 20 mg of cellobiose), then 500 mg potassium iodide and 5 ml of 1N sulfuric acid; the liberated iodine is converted to sodium hypoiodite by the addition of 0.5N sodium hydroxide (usually 10-12 ml)

to a pH of 11 to 12. The solution is left in the dark for 20 minutes, then acidified and the excess iodine titrated with 0.01N thiosulfate. Usually about 11.5 ml of thiosulfate are consumed per 20 mg cellobiose. Controls should be run frequently as the stoichiometry may vary with temperature or other factors.

In Fig. 8 is shown the rate of hypoiodite consumption with time; a leveling of the curve occurs after 20 minutes. The curve does not level completely, showing a slow but steady overoxidation. A plot of oxidations for several amounts of cellobiose gives a slope that is slightly higher than that demanded for a theoretical oxidation of cellobiose to cellobionic acid.

The addition of the alkali to the iodine solution to form hypoiodite is done in one stage, with a graduated pipet; toward the end of the addition the iodine disappears and the solution turns light yellow. It is best to check the pH in all cases, to insure that it is between 11 and 12.

The sugar must be added to the iodine system before the alkali is added; if the reverse addition is done, low values are often obtained. This is because the alkaline hypoiodite system rapidly disproportionates to iodate and iodide; this second system will not oxidize cellobiose, and so a low final thiosulfate titration is obtained. In most cases the sugar was added to the iodate, before the addition of potassium iodide and sulfuric acid to generate free iodine.

DETERMINATION OF BOROHYDRIDE WITH ALKALINE IODATE

This method, the oxidation of borohydride to borate with iodate in alkali, is very rapid, and the iodate consumed is determined by a subsequent titration with thiosulfate (10). Attempts were made to use this as a quenching agent for the flow reactor, but the amount of iodate used here is many times that needed for the hypoiodite determination of cellobiose in the system.

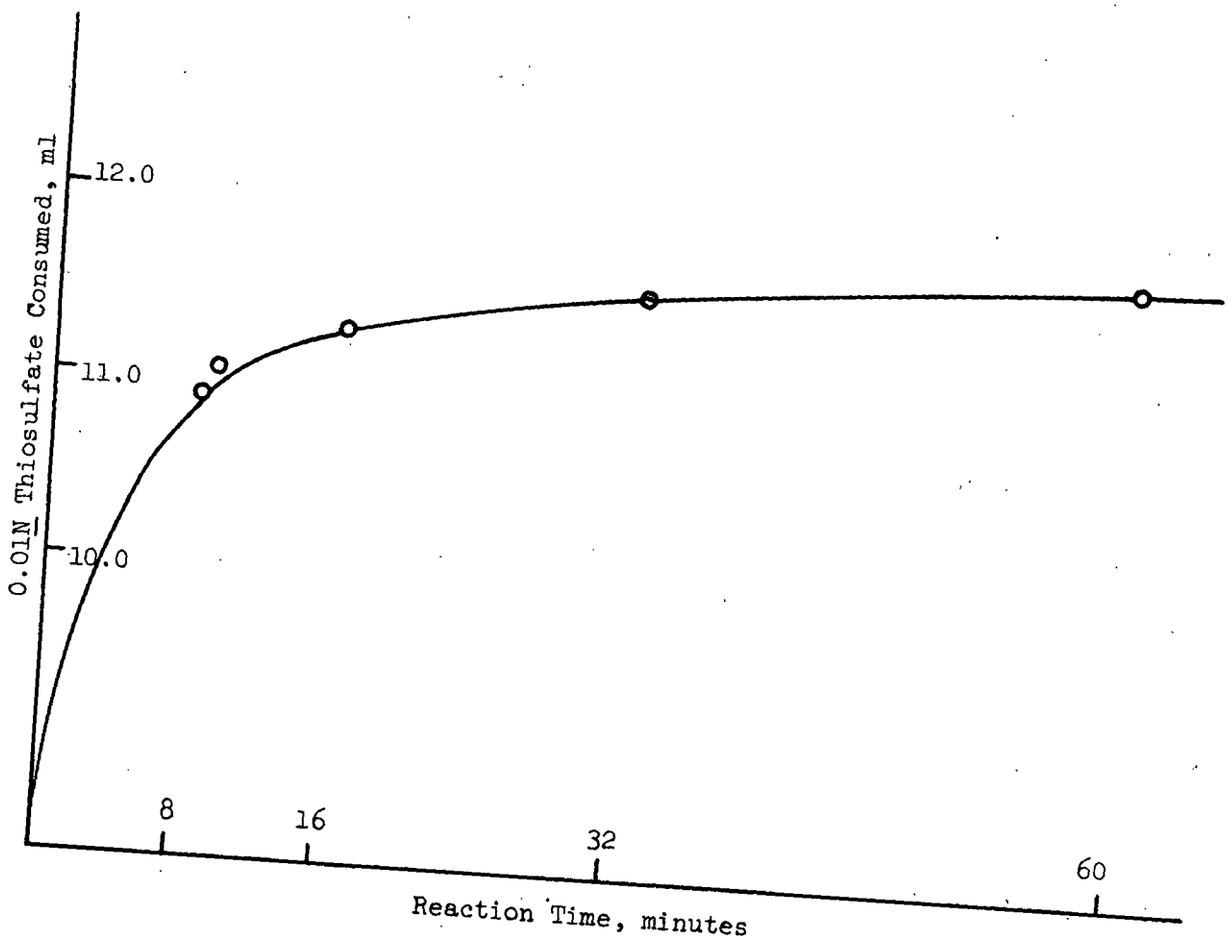


Figure 8. Oxidation of Cellobiose (20.05 mg) with Sodium Hypoiodite at pH 12.1

Another problem with iodate as a quenching agent is a possible oxidation of carbohydrates. An experiment with 120 mg of glucose and 10 ml of 0.25N iodate in 0.25N sodium hydroxide for 20 minutes showed a slight consumption of iodate, corresponding to about 10% of the original glucose. Another experiment, with fructose, showed no consumption of iodate.

REMOVAL OF BORIC ACID AND IODINE FROM THE SYSTEM

Borates have been shown to have an adverse effect on both the hypoiodite method and the PSA method, probably due to complexing with the sugars. Thus, borates reduced the consumption of thiosulfate in the hypoiodite method for cellobiose by approximately 50%.

It was found that if the system containing borates was adjusted to pH 5, subsequent concentration of the aqueous system to dryness and reconcentration with methanol would removal all the boric acid present. A quenched solution containing sulfuric acid and boric acid could thus be treated to give, at pH 5, a mixture of sodium sulfate and boric acid, and then by concentration, removal of the boric acid; analysis of the residue by the hypoiodite method proved to be satisfactory.

Adjustment of the pH to 7 also removed the borate present, but it was decided to use the region of 5 in the present work. In some cases pH values above 5 have been used, but never below.

Attempts were also made to remove free iodine from aqueous systems. Such a situation results when iodate is used to quench a kinetic sample; acidification will liberate iodine. This iodine could be removed only partly by several extractions with carbon tetrachloride. However, a better method was simply concentration of the aqueous system in vacuo at 50°C. The iodine distilled over with the water. This

was done by first adding potassium iodide and sulfuric acid to the iodate solution, then raising the pH of the acidic solution to 5. At this pH both the iodine and the boric acid were free and could be removed. However, it was found, by subsequent titration with thiosulfate, that a second concentration with water was often needed to remove the last traces of iodine.

While this method removes the iodine (from iodate originally) from an aqueous system, iodide ion is left. The latter ion is needed in excess, with acid, to convert iodate to iodine. Unfortunately, this conversion will not work unless iodide ion is in excess, and so the final system will always contain iodide ion.

EXPERIMENTAL PROCEDURES AND DATA

Kinetic Runs for Borohydride Reduction of Cellobiose

1. Run in flow reactor at 45°C.

Solutions were made up of: 1.50 g cellobiose/250 ml water
3.00 g sodium borohydride/250 ml of 0.02N sodium hydroxide
0.1N sulfuric acid for quenching.

Both the water and sodium hydroxide solution were boiled to remove air, then cooled. The sugar and borohydride were weighed to 0.01 g, and then washed carefully into 250-ml volumetric flasks via a funnel with a long stem touching the bottom of the flask. In this way air bubbles were avoided. After the two flasks were filled to the mark, a magnetic stirring bar was added, and the solution stirred carefully, so that a dimple appeared in the neck of the flasks. Vortexes were avoided, to prevent introduction of air.

In each reactor run, the empty reaction coils were immersed in the oil bath for 6 minutes, to equilibrate to the 45°C temperature. The following sequence was done.

1. Liquid from the syringes was pushed into the heating coils, and left 30 seconds.

2. The liquid was then pushed into the reaction coil, and left for a given period of time (0 to 6 minutes). The chart paper in the recorder was turned off during this period, measured to 1 second.

3. The quench stroke was then done manually. The quench solution was bubbly, from dissolved hydrogen, and had a pH of 1.6.

The total time of these operations could be read from the recorder chart, and the reaction interval added to this. Steps 1, 2, and 3 took about 20 seconds, so the zero time should be adjusted accordingly.

The quench solutions were adjusted with sodium hydroxide to pH 4.0, then concentrated to dryness, reconcentrated with MeOH to remove boric acid, and the dried residues dissolved in 30 ml of water, and analyzed by the sodium hypoiodite method for cellobiose, at pH 11 for 10 minutes.

The data obtained, given below, were erratic. The thiosulfate consumed is high, showing premature pushing of reaction solution into the quench line. Theoretically, 7 ml of reaction solution (= 21 mg cellobiose) should be in the quench system, and this should correspond to about 14 ml of 0.01N thiosulfate.

Time, minutes	0.01N Thiosulfate Consumed, ml
0	21.5
1	12.90
2	18.6
4	15.3
6	9.3

2. A second reactor run was made, with more success. The pH of the quench solutions, before concentration, was adjusted to 5.5.

Time, minutes	0.01N Thiosulfate Consumed, ml
0	10.1
2	10.9
4	7.1
8	5.0
16	3.5

The 0, 4 and 8 minute runs give a first-order plot; the other points are high.

3. Reduction of cellobiose at 45°C by sodium borohydride in water only; run in oil bath, not in flow reactor.

Two runs, were made with 20.8 mg cellobiose each, in 10 ml water. These were first heated 5 min in an oil bath, then 5 ml borohydride solution (40 mg) added. The reactions were stopped at 1.25 min and 2.25 minutes by addition to 100 ml of 0.1N sulfuric acid, giving a pH of 1.7 to 2.0.

The quenched solutions were adjusted to pH 5.5, concentrated to dryness, then with methanol, and analyzed by the sodium hypoiodite method at pH 11 for 10 minutes.

These two kinetic points, with the zero value gave a first-order plot. Another run was made at 4 minutes, giving a high value on the plot.

Time, minutes	0.01N Thiosulfate Consumed, ml	% Cellobiose Left
1.25	4.5	36
2.25	2.1	17
4.0	0.9	7.5

Handling Borohydride Solutions in the Flow Reactor

1. Quenching the borohydride with boric acid.

A solution was made up of 1.00 g sodium borohydride in 100 ml of 0.2N sodium hydroxide (boiled to removed air). This solution was run into both reaction syringes in the reactor, and 0.05M boric acid in the quenching syringes.

The borohydride solution was run through the heating and reaction coils and quenched with the boric acid. The quenched solution was immediately treated with 10 ml of 0.035N potassium iodate and 10 ml of 0.5N sodium hydroxide. This, after several minutes, was treated with potassium iodide and sulfuric acid, and the liberated iodine titrated. It was found that 15.6 mg of sodium borohydride was present in the quench out of 70.0 mg originally present in the reaction solution (7 ml). So quenching was only 80% complete.

A second run, with 0.125M boric acid gave a quench solution of pH 7.7, and 13.4 mg sodium borohydride left.

2. Quenching the borohydride with sulfuric acid.

Use of 0.1N sulfuric acid with the above system, gave pH 1.9, and zero thiosulfate consumed, so no borohydride was left.

Another run, with the reaction coils in an oil bath at 45°C for 30 seconds, gave a similar quench of pH 1.8 and no borohydride left.

3. Evolution of hydrogen from sodium borohydride solutions in the flow reactor.

A solution of 1.00 g sodium borohydride in 100 ml 0.1N sodium hydroxide was run into the reaction coil to the open end (the quench mixer was removed). In four hours at room temperature 3 drops of liquid were slowly formed out of the

open end, presumably caused by the slow evolution of hydrogen gas in the liquid in the coil. A similar experiment with 0.01N sodium hydroxide gave much faster decomposition. In 60 minutes about 700 mg of liquid was expelled into a tared test tube.

Sodium Hypoiodite Oxidation

1. 5-Ml aliquots (20.05 mg cellobiose) were run with 10.00 ml of 0.035N potassium iodate, converted to sodium hypoiodite at pH 12.1.

Time of Oxidation, minutes	Net Consumption of 0.01N Thiosulfate, ml
8	10.9
9	11.0
16	11.35
16	11.30
32	11.50
60	11.70
60	11.70

2. Titration of various amounts of cellobiose. Each sample was oxidized at pH 12.1 for 30 minutes.

Amount of Cellobiose, mg	Net Consumption of 0.01N Thiosulfate, ml
4.0	2.80
12.0	7.35
16.0	9.80
20.0	11.50

3. Titration of small amounts of cellobiose.

Amount of Cellobiose, mg	Net Consumption of 0.01N Thiosulfate, ml	Thiosulfate/ mg
3.29	2.17	0.6596
4.73	3.17	0.6702
5.41	3.46	0.6396
7.30	4.35	0.5959

4. Late addition of cellobiose to alkaline hypoiodite solution.

   A. Cellobiose (22.3 mg) was added first, then potassium iodate, potassium iodide, acid, and finally alkali to pH 11.5. Net thiosulfate consumed was 14.00 ml.

   B. Potassium iodate was added first, then potassium iodide, acid, then alkali to pH 11.5, and then after 5 minutes, the cellobiose was added. Net thiosulfate consumed was 4.40 ml.

Determination of Sodium Borohydride

1. 20-25 Mg of sodium borohydride was weighed out, dissolved in 25 ml 0.5N sodium hydroxide. Then 25.00 ml 0.25N potassium iodate was added, and stirred for 30 seconds. Then 2 g potassium iodide was added, followed by 20 ml 4N sulfuric acid, giving free iodine. This, after 3 minutes, was titrated with 0.1N thiosulfate.

   By this method, some "old borohydride" was found to be 87.1% pure. A second determination gave 89.4% purity. A conversion factor of 4.731 was used.

   mg Sodium borohydride = moles thiosulfate x 4.731.

2. Reaction of glucose with alkaline iodate.

   6 Mg glucose and 10 ml 0.25N potassium iodate and 10 ml 0.5N sodium hydroxide gave no change in subsequent thiosulfate titration after 23 minutes. But here the iodate is in very large excess.

   120 Mg glucose under the same conditions gave a difference of 0.6 ml titration of 0.1N thiosulfate, or about 10% glucose reaction.

100 Mg fructose under the same conditions gave no change in titer, for 15 minutes reaction time.

Removal of Boric Acid from Systems

1. Adverse effect of borates on sodium hypoiodite reaction.

   20 Mg glucose and 10 ml 0.035N potassium iodate (as sodium hypoiodite) gave 13.6 ml 0.01N thiosulfate consumed. But addition of 100 mg sodium borohydride to 50 ml water, addition of excess acid to decompose the borohydride, then addition of 20 mg glucose and analysis by the sodium hypoiodite method as above gave only 7.0 ml 0.01N thiosulfate consumed.

2. Titration of a mixture of sulfuric and boric acids.

   A mixture of equal volumes of 0.5N sulfuric and boric acids was titrated with 0.5N sodium hydroxide. The change in pH from 1.5 to 3.0 is slow, but 1-3 drops of sodium hydroxide then gave a fast shift to pH 5, showing an end point for sulfuric acid, but nonneutralization of boric acid.

3. Variation in pH for removal of boric acid.

   Two solutions were made up of 40 mg sodium borohydride in 5 ml of 0.5N sodium hydroxide; these were decomposed with 100 ml of 0.1N sulfuric acid, then 10 ml (20.4 mg) cellobiose solution was added. The solutions were adjusted to pH 5.2 to 5.3, and concentrated to dryness, then concentrated with methanol to remove boric acid.

   Two other solutions were made up similarly, but the pH adjusted to 7.1 to 7.2 for removal of the boric acid.

   Each of the four solutions was analyzed for cellobiose by the sodium hypoiodite method.

pH for Boric Acid Removal	Thiosulfate Consumed, ml
5.2	12.0
5.3	11.7
7.1	11.6
7.2	11.5

Removal of Iodine from Systems

Treatment of a borohydride system with alkaline iodate, and then liberation of iodine and titration with thiosulfate gave a solution containing iodide and tetrathionate. Addition of NaOH to pH 5.1 and concentration to remove boric acid gave a yellow residue and an odor of hydrogen sulfide.

Extraction of a similar solution, containing liberated iodine, at pH 5.1, with carbon tetrachloride, removed quite a bit of the iodine, based on color changes, but it was slow.

Finally, it was found that adjustment of the solution containing free iodine and boric acid to pH 5, and concentration in vacuo removed the free iodine quite rapidly in the aqueous distillate. Titration of the remaining solution with thio showed only a small amount of iodine left. Addition of more water and reconcentration removed the last of this.

OXIDATIONS WITH ANTHRAQUINONE SULFONIC ACIDS

EXPERIMENTAL RESULTS

The 1- and 2-anthraquinone sulfonic acids have been recommended as oxidants in alkaline solutions; they are presumably stable at high temperatures. The oxidation of polysaccharides end groups leads to stabilization and higher yields in alkaline pulping (11).

A few preliminary experiments have been carried out: oxidations of cellobiose for 10 minutes at 60°C in 0.1N sodium hydroxide. The resulting solutions were not amenable to analysis of the remaining cellobiose by the hypoiodite method (9). Apparently, the reduced forms of the anthraquinone sulfonic acids react readily with iodate or hypoiodite, so that high values of iodine consumption are obtained. This was confirmed by reducing the two acids with sodium borohydride; the resulting systems reacted readily with iodate or hypoiodite.

One oxidized sample was analyzed by gas chromatography, after conversion to the trimethylsilyl derivatives. However, no peak was obtained for cellobionic acid, only for the α and β forms of unreacted cellobiose. Many minor peaks were obtained, probably short-chain aldonic or saccharinic acids.

Originally, these oxidations were thought to be quite rapid, but oxidation may be directed toward fragmentation rather than selective oxidation of the end group. A combination of wet analysis (increase in iodine consumption) and gas chromatography is being considered for following the oxidations.

EXPERIMENTAL PROCEDURES

1. The anthraquinone sulfonic acid (1-AQS) sodium salt is only slightly soluble in water (400 mg/100 ml) whereas the 2-AQS salt is quite soluble. The potassium salt of 1-AQS is even less soluble, and addition of 0.5N potassium hydroxide to 200 mg 1-AQS sodium salt in 50 ml water gives a precipitate. In contrast, the 2-AQS potassium salt is quite soluble.

   Both Na salts have a pH of about 3.5 in water, and the solutions are light yellow to white. Alkali changes the color of 2-AQS to red, but 1-AQS does not change color with alkali.

2. An oxidation was carried out with 200 mg 1-AQS sodium salt
   50 ml 0.1N sodium hydroxide
   5 ml cellobiose solution (20 mg).

   The alkaline solution of 1-AQS was heated to 60°C, then 5 ml cellobiose solution added, and the mixture maintained at 60 for 10 minutes. It was then cooled to 10-20°C and analyzed by the sodium hypoiodite method for cellobiose.

   Back titration with 0.01N thiosulfate showed that 18.20 ml thiosulfate had been used. This was much higher than that needed for the original cellobiose (11.50 ml).

   A blank run was made by mixing 200 mg 1-AQS sodium salt and 20 mg cellobiose in 55 ml water and analyzing by the sodium hypoiodite method. 11.50 Ml 0.01N thiosulfate were consumed.

3. Iodimetric determination of 1-AQS and 2-AQS. 200-Mg samples of these were treated with 10.0 ml 0.035N potassium iodate, converted by acid to free iodine, and the latter titrated with 0.01N thiosulfate gave the theoretical amount, 34.50 ml. The same results were obtained by running 200-mg samples through the sodium hypoiodite determination.

Two solutions of 200 mg each 1- and 2-AQS in 50 ml 0.1N sodium hydroxide were heated 10 minutes at 60°C, then cooled and analyzed by the sodium hypoiodite method. The amount of thiosulfate consumed was 0.7 and 1.7 ml, respectively.

This was repeated, but with 20 mg cellobiose in each sample during the heating period. The amount of thiosulfate consumed in the sodium hypoiodite determination was 15.4 and 20.9 ml, respectively.

4. Reduction of AQS salts.

Samples of 200 mg each of 1- and 2-AQS sodium salts were treated with 80 mg sodium borohydride in 50 ml water for 90 minutes. Addition of sulfuric acid to the resulting bright red solutions destroyed excess borohydride and gave yellow solutions. Addition of sodium hydroxide to pH 9 gave a red color to AQS only.

Treatment of these reduced solutions with potassium iodate, conversion to free iodine, and titration of the latter gave 18.6 and 18.7 ml thiosulfate consumed.

5. Oxidation of cellobiose with less AQS.

These were done as for (2) above, with 20 and 40 mg of the acids. The thiosulfate consumed (for 20 and 40 mg, respectively) were 18.20 and 18.10 ml for the 1-AQS, and 19.0 and 21.0 ml for the 2-AQS.

ALTERATION OF FLOW REACTOR FOR SLOWER REACTIONS

INTRODUCTION

Originally the flow reactor was designed for reaction times from 30 seconds to 30 milliseconds approximately. This is a continuous operation, pushing liquid at a certain flow rate through a reaction coil of a given volume. The reaction time is directly proportional to the volume of the coil and inversely proportional to the flow rate.

In our Proposal No. 2068 for continuation of this project we suggested studying certain reactions involved in the early stages of the kraft cook. Some of these reactions, at lower temperatures, will probably be slower than the peeling reaction, with half-lives of several minutes rather than seconds. The switchboard of the flow reactor has been altered, so that liquid can be pumped into the reaction zone in an intermittent fashion, rather than continuously.

The removal of the reacted liquid from the reaction zone involves its displacement by unreacted liquid; ideally there should be very little mixing of the two types of liquid during this displacement. The extent of this mixing (plug flow) has been evaluated and is discussed below. This section involves some niceties of reactor operation that we were concerned about during the past project work, but did not check out, due to a matter of priorities.

The oscillograph recorder has been altered by the addition of two more channels, so that two thermistors (or thermocouples) can be placed in the reaction coils or at the mixers, and the temperature of the reaction solutions monitored simultaneously with the movements of the liquids from the syringes into the reactor.

INTERMITTENT FLOW AT LONG REACTION TIMES

This operation consists of six steps; they are given below, and steps (d) and (f) are shown in Fig. 9.

(a) Pushing the solutions (i.e., sugar and alkali) at a low flow rate into the heating coils (the "first" stroke).

(b) Heating the solutions for a given period of time.

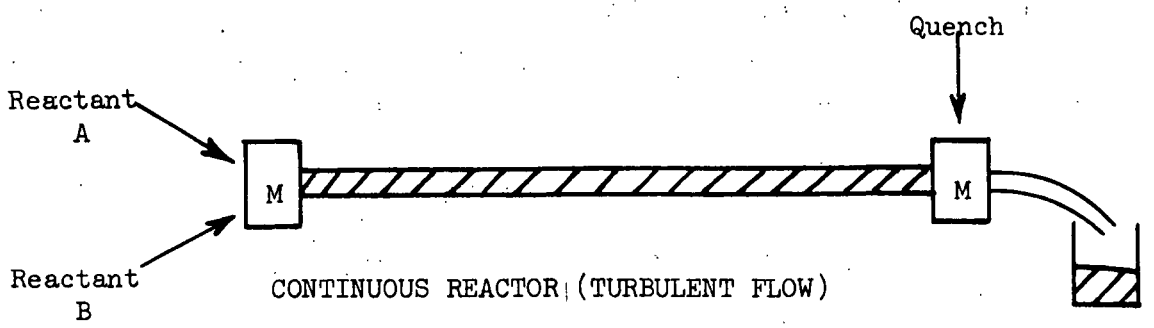
(c) Pushing the two heated solutions at a high flow rate through the first mixer and into the reaction coil (the "second" stroke).

(d) Stopping the flow so that the mixed solutions fill most of the reaction coil but do not reach the second mixer.

(e) Allowing this mixed reaction solution to remain in the reaction coil for a given period of time (30 seconds to several minutes).

(f) Pushing the solution out of the coil into the quench mixer at a high flow rate, with addition of quenching agent (i.e., acid) from another syringe (the "third" stroke).

This procedure differs from the continuous flow system normally used for faster reaction. In the continuous system, Steps (c) and (f) were combined as a "second" stroke, and Steps (d) and (e) were omitted; the first and second strokes each consisted of approximately 21 ml liquid. The microswitches have been altered now so that the "second" stroke is divided into a "second" and a "third" stroke. These two strokes, totalling 21 ml volume, can be regulated by movement of the second microswitch; the "second" stroke ranges from 1 to 11 ml volume, and the third stroke is the balance (remaining from 21 ml) or 20 to 10 ml volume. The details of the modified switchboard are given later in this report.



$$T_r = V/F = \frac{ml \times sec}{ml} = \text{seconds of reaction time}$$

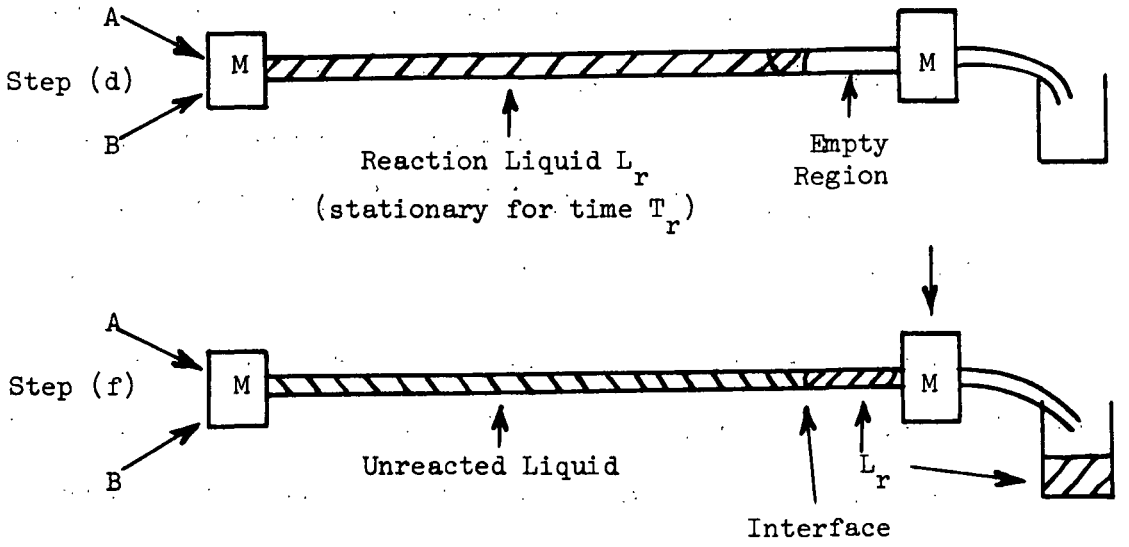


Figure 9. Comparison of Continuous and Intermittent Flow Reactors

It should also be mentioned here that these three strokes do not necessarily have to be operated in the same sequence. By "by-passing," only the second or third stroke can be used, or the third stroke can be used before the second or first stroke. The details of this "by-passing" are given later.

PROBLEM OF LAMINAR FLOW AT LOW FLOW RATES

The operation of the flow reactor in a continuous manner at low flow rates has been abandoned for slow reactions (above 30 seconds) for two reasons. First, the hydraulic system is not designed for slow movement of the rams, and movement of the syringes at such slow rates is accompanied by a chatter, an overcoming of the friction of the O-rings. Secondly, slow continuous flow of liquids through the reaction coil may well be accompanied by laminar flow (see Progress Report Four, page 32) and restricted movement of liquid regions near the walls of the coil. So an intermittent operation has been adopted for these slower reactions, with fast movement of liquid in and out of the reaction coil, to ensure good mixing.

PROBLEM OF PLUG FLOW

When a given volume of liquid in a coil or piece of tubing is displaced, this displacement is done by introducing a second volume of liquid, driven from a syringe. In the continuous flow reactor, cold liquid from the mixing syringes displaced hot liquid in the heating coils, and this hot liquid was driven through the reaction coil. In the present intermittent operation, liquid in the reaction coil will be displaced by nonreacted liquid from the heating coils. In this latter case it is very important that very little of the first liquid, which is unreacted or has no kinetic history, mix with the reacted liquid being displaced.

To insure this nonmixing, or minimum diffusion at the interface [see (d) and (f) in Fig. 9] only part of the reaction liquid is driven out of the coil; the remaining liquid forms a buffer zone and is not collected for subsequent analysis. The effectiveness of this buffer zone was determined by displacing water from a coil with 1N sodium hydroxide and titrating the water with 0.1N hydrochloric acid to determine the amount of diffusion occurring. The data, for two buffer zones and for two temperatures, are given in Table III and shown in Fig. 10.

For a buffer zone of 2 ml, there is very little diffusion of the alkali into the water zone, but for 1 ml the diffusion is appreciable, up to 2.2% at 90° and for a period of one hour. This diffusion is greater than anticipated. The 1-ml zone represents a 10.8-inch length of narrow tubing, and the diffusion is upward; the denser alkali is the lower zone in a vertical reaction coil.

In summary, one can conclude that the diffusion falls off with the length of coil, but increases with temperature (lower viscosity of water) and also with time. The temperature effect is shown clearly for the 1-ml buffer zone, but for the 2-ml zone the data are less exact. In the latter case we are dealing with very small amounts of alkali, and the precision is lower.

Based on these data, it seems advisable to use a 2-ml buffer zone in kinetic experiments, to keep errors in kinetic samples to a minimum.

EXPANSION OF LIQUID IN TUBING DURING HEATING

The position of liquid (i.e., water) in the various coils at certain stages of flow can be readily determined at room temperature, by either measuring the internal volumes of the tubing and the volumes of liquids involved, or by

TABLE III

DIFFUSION OF ALKALI INTO WATER

	Acid Titration of Water Displaced for 1-ml gap	for 2-ml gap
Displacement of water at 25°C	0.7 ml	0.05 ml
Similar, but with 30-min time interval	--	0.15 ml
Similar but for 60 min	1.5 ml	0.30 ml
Displacement of water at 90°C and 3 min heating time	1.8 ml	0.05 ml
Similar, but 60 min heating time	2.2 ml	0.05 ml

Note -- the acid titration is in ml of 0.1N hydrochloric acid; a similar titration of the 9 or 10 ml, respectively, of 1N sodium hydroxide used as a displacement liquid would be 90 and 100 ml approximately. Flow rates were 0.5 to 1.6 ml/sec.

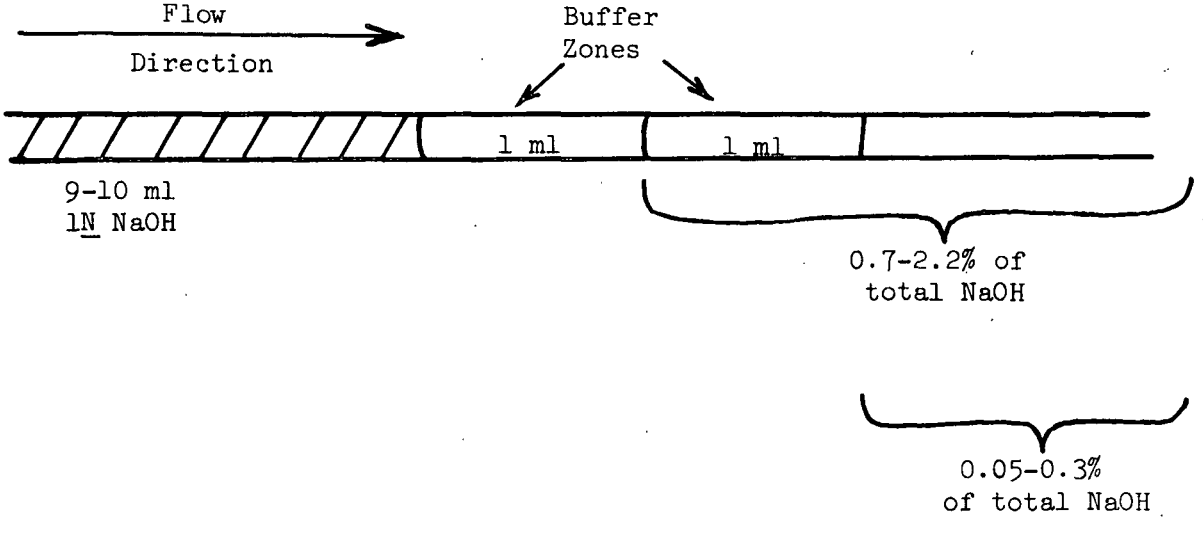


Figure 10. Extent of Diffusion of Alkali into Aqueous Zone

(The figure is not to scale; the 1-ml zones are each 10.8 inches in length and 0.085 inch inside diameter.)

noting the time required for a given volume of liquid to emerge from the end of a section of tubing. For higher temperatures, especially above 100°C, and under pressurized conditions, allowances have to be made for the expansion of the liquid, i.e., increase in specific volume.

As a check on this expansion, a given system of two heating coils, one mixer and one reaction coil was filled completely with deaerated water at 25°C. The weight of water in this system was approximately 34.10 g (= ml approximately). The system was then immersed in an oil bath at 90°C and the liquid emitted from the end of the reaction coil carefully collected in a weighing bottle. Two such experiments gave an average weight of 1.030 grams. The calculated change in volume (change from a specific volume of 1.003 to 1.0359) is about 3.3% or for 34.1 ml volume this would be 1.125 grams. So the amounts found are near the expected value.

The water used in these experiments was deaerated by boiling distilled water for 5 minutes and then cooling to room temperature. The time for thermal expansion was 3.5 minutes, and most of this was in the first 1.5 minutes. See Table IV.

TABLE IV

RATE OF THERMAL EXPANSION OF WATER FROM 25 TO 90°C

Time Interval, sec	Drops of Water	Drops per Minute
0-30	13+	26+
30-60	5	10
60-90	3	6
90-210	4	2
210-360	0	0

At first these experiments were carried out with distilled water that had not been deaerated, and two adverse effects occurred. First, the amount of water emitted was too great, of the order of 2.3 to 2.6 g. Secondly, this water was emitted steadily over a period of 15 minutes. Obviously, air was being expelled slowly from the water during heating, and the air pockets formed in the tubing expelled an excessive amount of water. In contrast, the deaerated water expanded during a short period of time, that expected for thermal equilibration.

In the kinetic experiments carried out earlier on this project under pressurized conditions, no attempt was made to insure that all aqueous solutions were deaerated. However, under pressurized conditions (30 to 150 psig nitrogen) there should be little tendency for the small amount of air dissolved in the water to escape. Only the oxygen (about 20%) in the dissolved air will be a factor. The amount of dissolved nitrogen in the solutions will actually increase, due to the applied nitrogen pressure. The quenched solutions removed from the reactor tend to bubble quite strongly when stirred at room temperature, showing the presence of this dissolved nitrogen.

DIFFUSION OF LIQUIDS AT THE MIXER

Ideally, the two liquids should meet at a point source at the mixer, but in practice, they pass through two Swagelok fittings, attached to a stainless steel block, and meet, via a 1/8-inch ID hole, at a splitter (Fig. 11). From this splitter the liquid is led through the jet mixer into the reaction coil. The splitter serves to reduce the volume at the Tee to a minimum, but there still can be diffusion at this junction. The volume of the jet mixer is very small and the openings in this mixer are also small, of the order of 0.04-inch ID. So diffusion will be occurring primarily at the splitter, and will give some pushing liquid

that is partially reacted. The jet mixer will serve as a constriction and limit diffusion into the reaction coil.

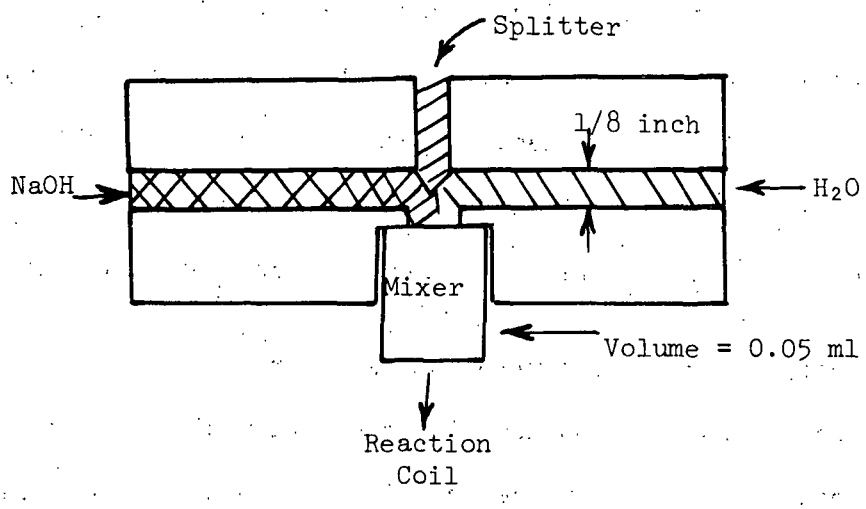


Figure 11. Upper Cap Housing Jet Mixer

The effect of time on such diffusion is shown in Table V. Initially, both 2N sodium hydroxide and water were driven from heating coils (at 25°C) through the mixer and then through a short delivery tube into a beaker. Then only the water syringe was operated to wash all the alkali out of the lower part of the mixer and out of the delivery tube. Several such washes reduced the alkali to a minimum; these washings, each of about one minute, and during this period there was undoubtedly diffusion from the alkali side of the mixer. Then the liquid flow was stopped for a given period of time, and, as shown in Table V the amount of alkali in subsequent water washes rose appreciably.

TABLE V

DIFFUSION OF ALKALI ACROSS THE MIXER

Time of Diffusion (min)	Alkali on Water Side (as ml of 0.1N HCl)
1	0.10
15	0.30
30	0.45

In summary, one might say that there are no sharp points at junctions of different types of liquids; there is always a slow but steady mixing of liquids in the mixer, with zero flow rate, and also a slow but steady mixing of liquids during the displacement process in the reaction coil. The best way to correct for these effects is to allow a certain buffer zone and to take only part of the reaction liquid as a sample for subsequent analysis.

MODIFICATION OF THE SWITCHBOARD

In the original design there were two microswitches with different functions. The first one automatically stopped the movement of the mixing ram at a half-way point (delivery of half of the 20.7 ml from each of the mixing syringes); it divided the total movement of these syringes into two "half-strokes." A manual switch was then used to complete the second half-stroke.

The second microswitch was designed to turn on a circuit (the quench ram) when a given movement of the mixing ram (or mixing syringe) occurred during its second "half-stroke." This given movement corresponded to the pushing of 1 to 11 ml of liquid into the reaction coil. Now this microswitch has been altered by adding a mix-ram setpoint switch, and it can be used to stop the mix ram when this same volume (1 to 11 ml) has entered the reaction coil (Step d in Fig. 1). The operation of the switchboard is described later in this report, and details of the wiring in Fig. 4. Thus, the new switchboard can be used either for a continuous or an intermittent flow reactor.

It should be pointed out that the new arrangement splits the second half of the hydraulic ram movement into two parts; these two parts comprise a total volume of about 21 ml. So now we have three strokes or movements of the mixing ram (or the two mixing syringes). (See Fig. 9.) The first, as usual,

is 20.7 ml; the second is 1 to 11 ml [Step (c)] and the third is 20 to 10 ml [Step (f)].

TECHNIQUE OF CHECKING DIFFUSION OF ALKALI INTO WATER

For this procedure a reaction coil of about 11 ml volume was attached to a mixer and two heating coils; the latter are connected to two mixing syringes containing sodium hydroxide and water. The end of the reaction coil (0.085 x 120 inches) was attached to a short delivery tube of about 0.2 ml volume. The essential arrangements and sequence of operations are shown in Fig. 12, and the manipulation of valves, etc., given in detail below. The two heating coils (not shown in Fig. 12) and the reaction coil were mounted vertically, so that liquid flow was upward, to displace air and prevent formation of air bubbles within the coils.

Filling operation (Fig. 12-1). The two syringes were filled with 2N sodium hydroxide and water (full retraction of ram, with valves at FV position), then these liquids pushed (CV position) through the heating coils and mixer (total volume of these is 25 ml) and into the reaction coil. This was repeated by refilling the syringes and driving the solution through the coils again as above. The reaction coil now contains 1N sodium hydroxide.

Washing operation (Fig. 12-2). The sodium hydroxide syringe was by-passed (FV) and the water syringe repeatedly filled (FV) and water then pushed (CV) through the reaction coil. Five such washings gave a final effluent equivalent to 0.05 ml (one drop) of 0.1N hydrochloric acid. At this stage we have water in one heating coil and in the reaction coil, and 2N sodium hydroxide in the other heating coil.

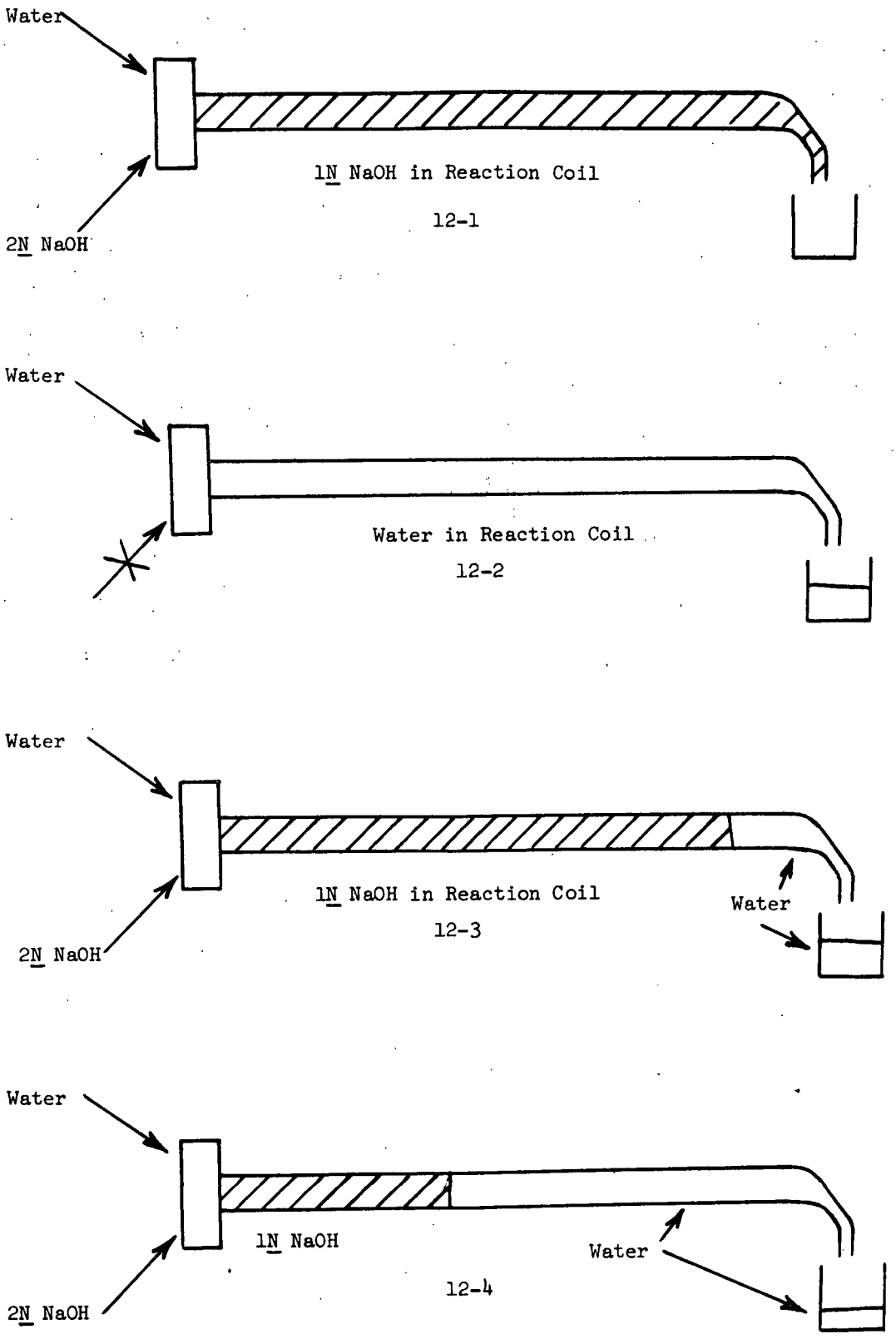


Figure 12. Sequence of Operations for Monitoring Diffusion of Alkali into Water

Displacement operation (Fig. 12-3). The two syringes are filled (FV) and then they are by-passed (FV) to the Center position. They are then advanced (CV) to the Past Center position, the second stroke. This stroke has been adjusted in advance to deliver either 9 or 10 ml of solution from both syringes. In this manner the reaction coil is partly filled with 1N sodium hydroxide and a certain volume of water is collected for subsequent titration.

Partial displacement process. (Fig. 12-4). For this the Past Center switch is turned on for a period of time sufficient to advance the syringes about half-way through the second stroke. With a flow rate of about 0.6 ml/sec this will take about 8 sec. The switch is then turned off and the system left for a given period of time. The switch is then on to complete the Past Center stroke and we end up with the situation given in Fig. 12-3. (Sequences 1,2,4 and then 3). During this interval there is extended contact of alkali and water in the middle of the reaction coil.

Operations at elevated temperatures. These are done as described above, except that the system is given a minimum of 3 minutes for thermal equilibration (at Stage 2) or a longer period of time at Stage 4. There will be some expansion of liquid during the heating period but the volume will be 1 ml at the most.

OPERATION OF THE MODIFIED FLOW REACTOR

The flow reactor consists primarily of a series of two heating coils and one reaction coil, connected to two mixers. The reactant solutions are heated to a certain temperature, then driven through a mixer into a reaction coil, at a certain flow rate, and this reaction solution is then quenched at a second mixer by addition of a third reactant.

FUNCTION OF THE SWITCHBOARD

The switchboard, shown in Fig. 13 and 14, controls the movement of these solutions; its functions can be divided into four parts.

(1) Hydraulic ram switches. These control the starting and stopping of hydraulic rams, which force liquid out of syringes into the coils, or else by a retraction process draw liquid into the syringes, as a filling operation. There are two types, manual and automatic; the latter are operated by microswitches. The wiring diagrams are shown in Fig. 15.

(2) Flow control devices. These are micrometer needle controls, which regulate the rate of flow of hydraulic oil into the rams, and thus the rate of movement of liquid from or into the syringes.

(3) Monitoring the position of the hydraulic rams and the rate of their movements. This is done by the use of linear potentiometers, connected to each ram; their movement is shown by two small lights (traces) moving back and forth on an oscillograph recorder. The recordings of this light movement on photographic paper give a trace of the X-Y type (the paper moves at a rate ranging from 0.1 to 80 inches a second).

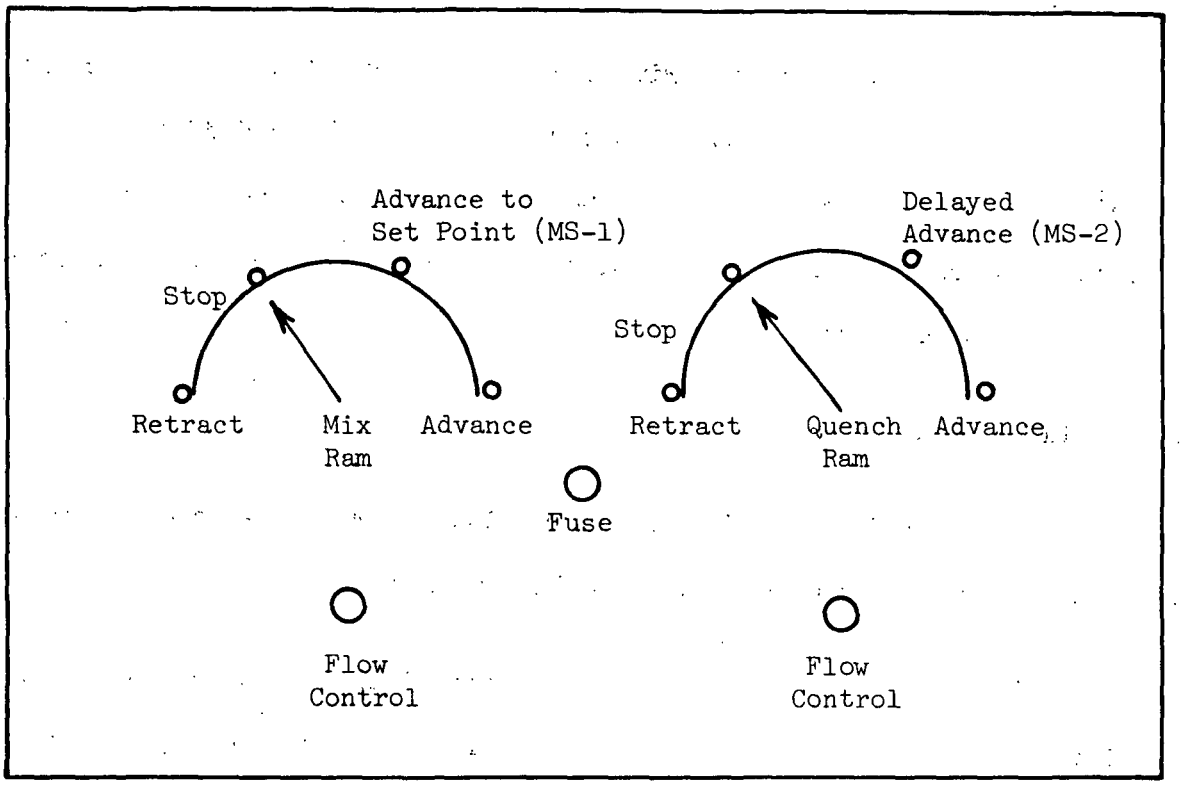


Figure 13. Details of Lower Switchboard.

This switchboard, with the Center to Past Center switch (MS-3) on the Upper Switchboard, controls the motions of the two rams, and the flow of liquids from the syringes into the heating and reaction coils.

The switches are of two types:
1. Manual switches. These are Retract, Stop, and Advance.
2. Automatic switches, labeled MS-1, MS-2, and MS-3.

The two flow regulators are a micrometer type, to control the rate of flow of hydraulic oil to and from the rams. They should not be closed below 025, as the needles may stick.

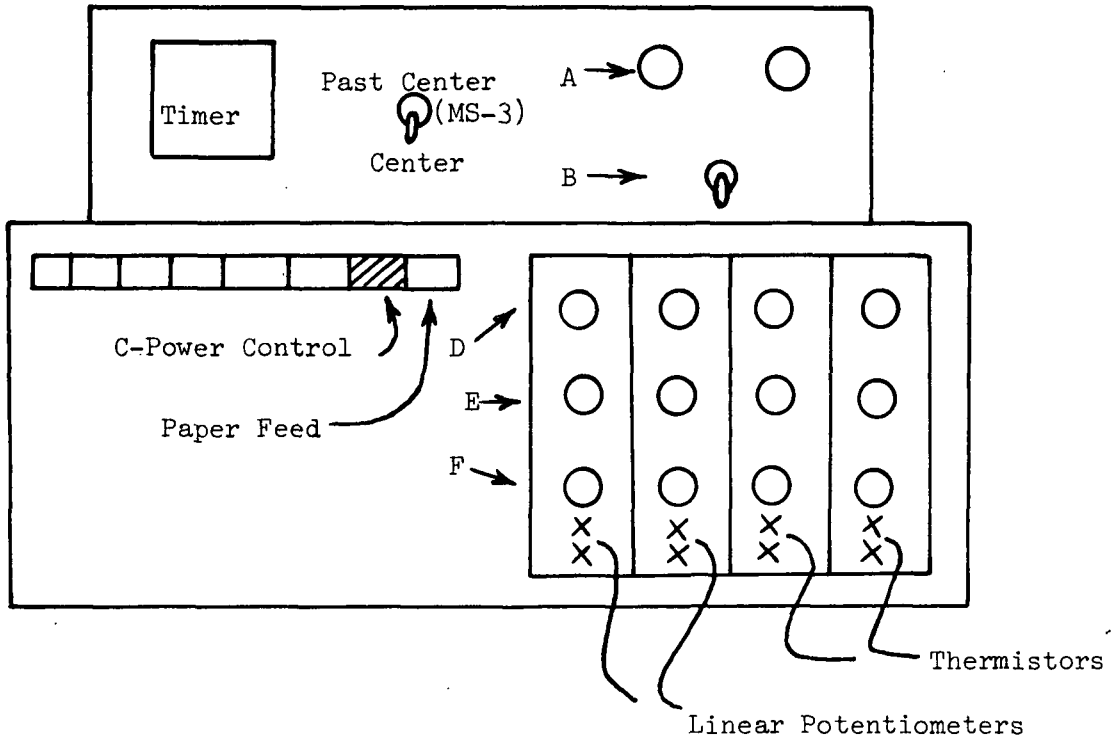


Figure 14. Oscillograph and Upper Switchboard

A Rheostats for position potentiometers
B Switch for A; up is on
C Power switch on oscillograph recorder
D Step range switch on differential amplifier; this is a gain control
E Continuous range switch
F Zero adjustment for base line

Steps 1-6 below are for adjustments of the two amplifiers on the left, connected to the mix and quench rams. For the thermistors connected to the two amplifiers on the right, adjustments in position are made on balance potentiometers (not shown) and with a final gain control (Switch D) setting of 1.0.

1. Turn on B and C; retract rams on lower switchboard
2. Set D to "off"
3. Adjust F to base line (sensitive)
4. Set D to 50, then adjust A to base line
5. Advance rams
6. Adjust E to give span desired. (Maximum is 6 inches.)

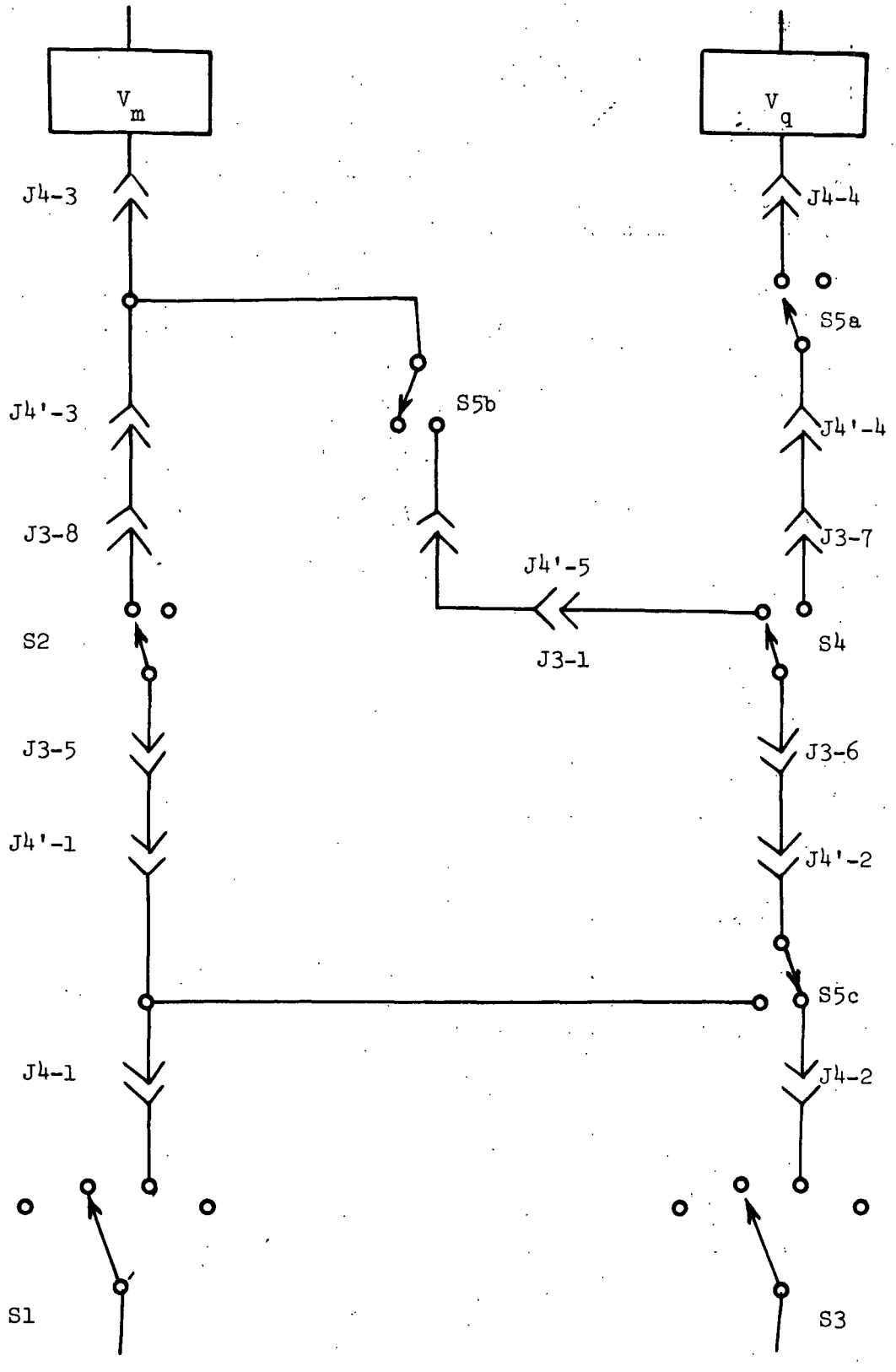


Figure 15. Wiring Diagram for Modified Switchboard.

(4) Measuring the temperature of the liquid moving through the coils, after being heated in an oil bath. A thermistor, mounted in the flow line, is connected to the oscillograph, and the displacement of a trace light on the latter will show any change in temperature.

CONNECTION OF SYRINGES TO REAGENTS AND TO HEATING COILS

The several syringes are connected by two-way stainless steel valves to both the bottles containing reagents and to the heating coils. The syringes thus can operate in a filling mode (FV), connected to the reagent bottles, or in a reaction mode (CV), connected to the heating coils. The latter adjustment of the two-way valve is shown in Fig. 16. The valve cannot be operated to connect the reagent bottle and heating coil; this avoids siphoning of reagent into the flow reactor.

In the description of switchboard operation below, the position of the valve is given after each paragraph heading.

OPERATION OF HYDRAULIC RAM SWITCHES

Three of the four switches for each ram (Fig. 13) are of the manual type. The retract switch pulls the ram backward, and similarly the piston in each syringe; in this way liquid is sucked into the syringe, as a filling operation. The advance switch conversely advances the ram and syringe, and liquid is forced out of the syringe.

The movement of the two rams in either direction is stopped automatically by the piston within the ram hitting the end of the cylinder. We can stop either ram in between these two extremes by using the stop switch; however, manual use of this switch will give only an approximate intermediate position, and the use

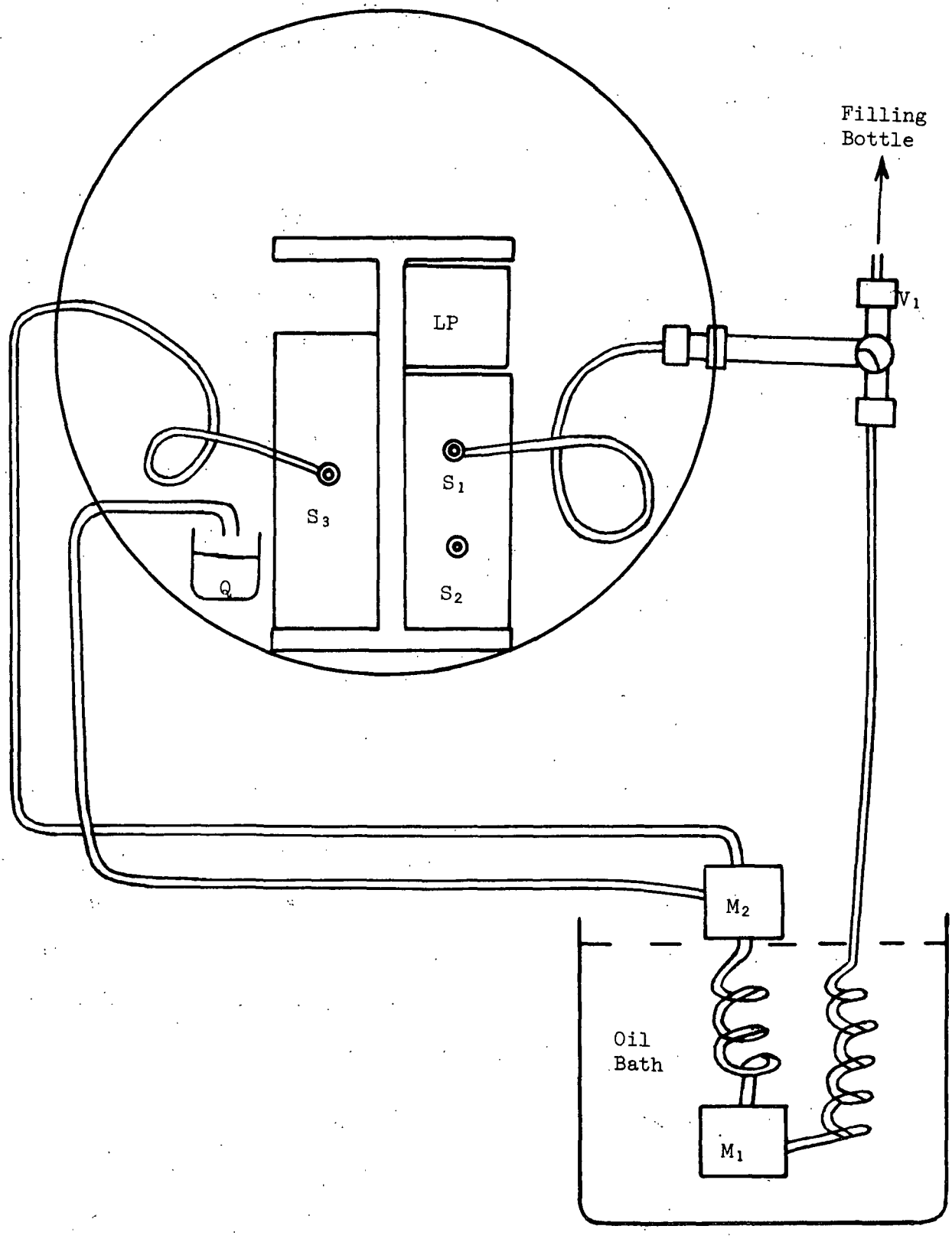


Figure 16. End View of Flow Reactor Connected to Syringes in Pressure Chamber

Note: Valve Connections to S_2 and S_3 are Omitted

of microswitches, described below, will give precise positions. Use of these two manual switches for filling the syringes and emptying, will deliver definite and reproducible quantities of liquid (20.7 ml for each mix syringe and about 98 ml for the quench syringe).

Three automatic switches (MS-1 and MS-2 in Fig. 13 and MS-3 in Fig. 14), in conjunction with two microswitches, allow the movement of the mix ram to be divided into two or three parts, and also allow the coordinated movement of the quench ram relative to that of the mix rams.

The best way to describe the use of these several switches is to give examples of the possible arrangements, and the subsequent flow of liquid. They are described below and typical operations are listed in Table VI, with numbers referring to details in the text.

(1) Filling a syringe (FV). The syringe is initially in an advance position; i.e., it is empty. The hydraulic pump is started (220-volt switch on the wall), and the ram switch is turned to retract. With a flow setting of 075, it will take about 30 seconds for a mix syringe to fill with 20.7 ml of liquid. Generally, the syringe is filled and emptied back into the filling bottle several times to drive any air out of the tubing or syringe. It is also advisable to wait 30 seconds after the retract action is finished, to insure that all the liquid is sucked into the syringe. Often the ram will retract faster than liquid can enter, and so a little time is needed at the end of the stroke.

(2) Emptying a syringe (CV). The advance valve is turned on; liquid will then be driven out of the syringe into the system of coils. The total amount will be 20.7 ml for each mix syringe and 98 ml for the quench syringe. By use of a two-way valve the liquid can be either directed into the coils or else (FV) will

TABLE VI

MOVEMENT OF LIQUID IN SYRINGES

Mix Ram Switch	MS-3 Switch	Quench Ram Switch	Mix Syringe	Quench Syringe	Operation No.
Retract	Immaterial	Retract	Full, 20.7 ml	Full, 98 ml	1
Advance	Immaterial	Advance	Empty	Empty	2
Retract	to Center	Stop	Full, 20.7 ml	No movement	1
Advance to Center (MS-1)	to Center	Stop	Half stroke, 10.35 ml	No movement	4
Advance	to Center	Stop	2nd half stroke, empty	No movement	5
Retract	to Center	Stop	Full, 20.7 ml	No movement	1
Advance to Center	to Center	Stop	Half stroke, 10.35 ml	No movement	4
Advance to Center	to Past Center	Stop	Second stroke, 1 to 6 ml removed	No movement	6
Advance	to Past Center	Stop	Third stroke, 9.35 to 4.35 ml removed	No movement	7
Retract	to Past Center	Stop	Full, 20.7 ml	No movement	1
Advance to Center	to Past Center	Stop	10.35 + (1 to 6 ml) removed; 1st and 2nd strokes	No movement	8
Retract	to Center	Retract	Full, 20.7 ml	Full, 98 ml	1
Advance to Center	to Center	Delayed Advance	Half stroke, 10.35 ml	Full, 98 ml	4
Advance	to Center	Delayed Advance	Second half stroke, 10.35 ml	98 ml out (at certain stages of 2nd half stroke)	9

Note — For filling procedure, a two-way valve is set in fill (FV) position; for movement into coils, this valve is set to the coil position (CV).

be returned to the fill bottle or a rinse bottle. The latter operation is the by-pass technique described below.

(3) Intermediate manual position (CV). The emptying of a syringe can be stopped in an intermediate position by simply turning the switch to advance first, then turning it later to the stop position. This latter action should be done before the stroke is completed. However, such a procedure is not very accurate, as the movement of the ram (seen on the oscillograph) cannot be judged visually in a precise manner. So this procedure is seldom done.

(4) Half-stroke advance of the mix ram (CV). This is done by first setting MS-3 to the center position, then turning the mix ram switch from retard (the syringe is filled) to the MS-1 position (advance to set point). The ram will advance one-half stroke; it is then stopped by a microswitch, and only 10.35 ml of liquid will be driven out of the syringe. The position of this microswitch is fixed and divides the movement of the mix ram into two equal parts.

(5) Second half-stroke of the mix ram (CV). Changing from MS-1 to advance will advance the mix ram a second half-stroke, delivering another 10.35 ml.

(6) Past Center stroke of the mix ram (CV). If MS-3 is changed from center to past center, after Step (4) has been carried out, the mix ram will advance only part of the second half-stroke and then stop. This advance is regulated by an adjustable microswitch, and ranges from 1 to 6 ml in volume. (For the two syringes the amount will be twice this volume.)

(7) Third stroke of the mix ram (CV). This, after Step (6) is completed, is done by turning the manual switch to advance. The volume of this third stroke will be the remainder of the 10.35 ml remaining in the syringe, and will range

from 9.35 ml down to 4.35 ml. The past center stroke and this third stroke of course will total 10.35 ml.

(8) Combined half-stroke and past center stroke (CV). This, though seldom used, is done by first filling the syringe (switch to retract), turning MS-3 to past center, and then the mix ram switch to MS-1. The ram will advance through the center stage until the second microswitch stops the movement. The volume delivered will be 11.35 to 17.35 ml.

(9) Coordinated movement of mix ram and quench ram. This arrangement is done to cause quenching of solutions during fast reactions, i.e., fast movement of both rams. Both mix and quench syringes are filled, and half of the mix syringes emptied into the heating coils. (MS-2 switch used, with MS-3 at center position.) Then the MS-2 switch (Delayed Advance) on the quench ram is turned on; the quench ram will not move. The mix ram switch is changed to the advance position, and the ram will complete the second half-stroke. During this stroke the ram movement will engage the second microswitch and automatically turn on the quench ram. Thus, we have a coordinated movement of reaction solution out of the reaction coil into the second mixer, and simultaneous movement of quench solution into the mixer also. This arrangement, described in earlier reports, can be adjusted by movement of the microswitch, to start when as little as 1 ml of liquid has entered the reaction coil. Both reaction liquid and quench liquid should meet simultaneously at the second mixer. A certain amount of overlapping is allowed, i.e., quench liquid enters the mixer first, to insure stopping of the reaction at the right time.

(10) Manual quenching. For very fast reactions, with small reaction coils, the second microswitch cannot be adjusted below 1 ml movement of the mix

ram. So the two switches are operated manually; the quench switch is first turned from Delayed Advance to Advance, and then the Mix Ram switch from MS-1 to Advance. With practice of this manual operation, the quench syringe can be started slightly before the mix syringes.

(11) By-passing technique (FV). If one of the syringes has its valve set to a FV position and the other to a CV position, and the two syringes are advanced (by movement of the mixing ram), only the second syringe will push liquid into the coil system. The first syringe will simply return liquid to the filling bottle; it has been by-passed or is in a neutral attitude. Thus, we can operate either one of the syringes independently.

Similarly, we can by-pass any one or two of the three strokes of the mixing ram by adjusting the valves accordingly. The syringes can be filled (FV), the ram advanced (FV) to the Center position (first stroke of 10.35 ml), the valves changed to the CV position, and the syringes advanced to Past Center to push a limited amount of liquid into the coils during the second stroke. Or the first two strokes can be by-passed and only the third stroke (20 to 10 ml) used.

Both of these techniques have been made use of in the study of diffusion of alkali into water.

FLOW CONTROL REGULATORS

These two flow devices, when completely open, divide the flow of oil from the hydraulic pump into two parts: two-thirds of the flow for the quench ram, and one-third for the mix ram. The maximum rate of flow for each mixing syringe is about 15 ml/sec and a detailed flow setting is given in Table VII. The maximum flow rate for the quench syringe is about 50 ml/sec. In practice the latter is adjusted so that the flow rate is about 5-10 times that of the mixing syringe.

TABLE VII

FLOW RATES FOR MIXING SYRINGES[a]

Control Setting	Flow Rate, ml/sec
030	0.13
042	0.41
060	0.90
075	1.60
100	3.0
140	5.2
225	9.2
300	14.2

[a]The above flow rates are for two syringes working together, or represent the flow of reaction solution, not individual reactants.

Initially, when the hydraulic pump is started up, the oil is cold and the flow rate is at a minimum; after a few minutes the oil warms up and the flow rate increases, so that the data in Table II are approximate.

In kinetic work the flow rate of the mixing syringes is the limiting factor; the rate of movement of the quench syringe is adjusted (by recording it on a photographic trace) so that it brackets the reaction liquid coming out of the reaction coil. It is not important to know the absolute speed of the quench syringe, as long as an excess of quenching agent is in contact with the reaction solution at the second mixer.

When the hydraulic pump is first turned on, there may be some air in the oil line. This air is bled out, by suitable valves, at the end of an advance stroke of either ram (i.e., when pressure in the line is at a maximum). Some oil is removed from the line at the same time and is drained into a beaker.

Normally the hydraulic pump is operated only when a kinetic run is being made, and is shut off otherwise. However, it has been found best to keep the pump going while the reactor is under pressure, to prevent backward movement of the syringe pistons. The pressure of the hydraulic pump (up to 1000 psig) is more than enough to overcome the nitrogen pressure on the reactor (up to 180 psig).

MONITORING RAM MOVEMENTS WITH THE OSCILLOGRAPH

The controls for the oscillograph are shown in Fig. 14; they are connected with the upper switchboard. This recorder has four differential amplifiers; two of them are connected each to a trace light and to a linear potentiometer. The latter is connected mechanically to the piston ram of a given hydraulic ram. Movement of the ram is shown by a corresponding movement of the trace light. This movement can be observed visually in a window on the oscillograph or recorded on a piece of moving photographic paper. The details of adjusting the circuits for base-line and span of trace movement (6 inches maximum) are given on Fig. 14.

Usually the chart paper speeds range from 0.2 to 2 inches per second. For speeds up to 0.8 inch per second, the paper is marked (by a series of flashing lights) at one-second intervals. For speeds from 1 to 8 inches per second the intervals are one-tenth of a second. Higher chart speeds (up to 80 inches per second) are marked at one-hundredth of a second; these speeds have not been used in the present work.

For filling operations, the movement of the rams (Advance or Retract positions) are observed visually; in actual kinetic runs the recording of trace movements on photographic paper is used to give a time dimension.

The electric timer is used with the oscillograph for long runs, to avoid excessive use of paper. The paper trace can be employed for the first and last minute of a run, for mixing and quenching, and is stopped during the intermediate period (Fig. 17).

Normally we are only interested in the extreme movement of the rams and their rate of movement; the trace will show the starting and stopping of the rams and the time scale. The chart paper, 6 inches wide, has a series of 60 horizontal lines; these can be used to show the position of the rams at any given time. However, this is not done; the microswitches control the flow of definite intermediate volumes, determined by collection and weighing.

THERMISTOR SENSING UNITS

These units (thermocouples also) are mounted in stainless steel Tees (see Fig. 18) through a 1/4-inch pipe thread fitting; the Tees also have two 1/8-inch Swagelok fittings for connection to the flow reactor. The gain of Switch D, originally at 1/50 for adjustment of the intermediate potentiometer to place the trace light on the chart paper, is finally changed to 1.0 to obtain the maximum sensitivity for the thermistor. With this gain of 1.0, the vertical movement of the trace light (6 inches) corresponds to 6°C. Each of the 60 horizontal lines on the recorder is 0.1°; this seems to be linear.

The housing of the thermistor, a Swagelok Tee, has a certain amount of mass, and heat transfer into this mass takes from 3 to 5 minutes (for a bath at 90°C). In contrast, preliminary experiments with the heating coils, with lighter walls, containing water at 90° show that only two minutes are needed to bring the water to within 0.5 degree of the ambient temperature. So it may be best to heat the system of coils and thermistor in an empty condition first, then

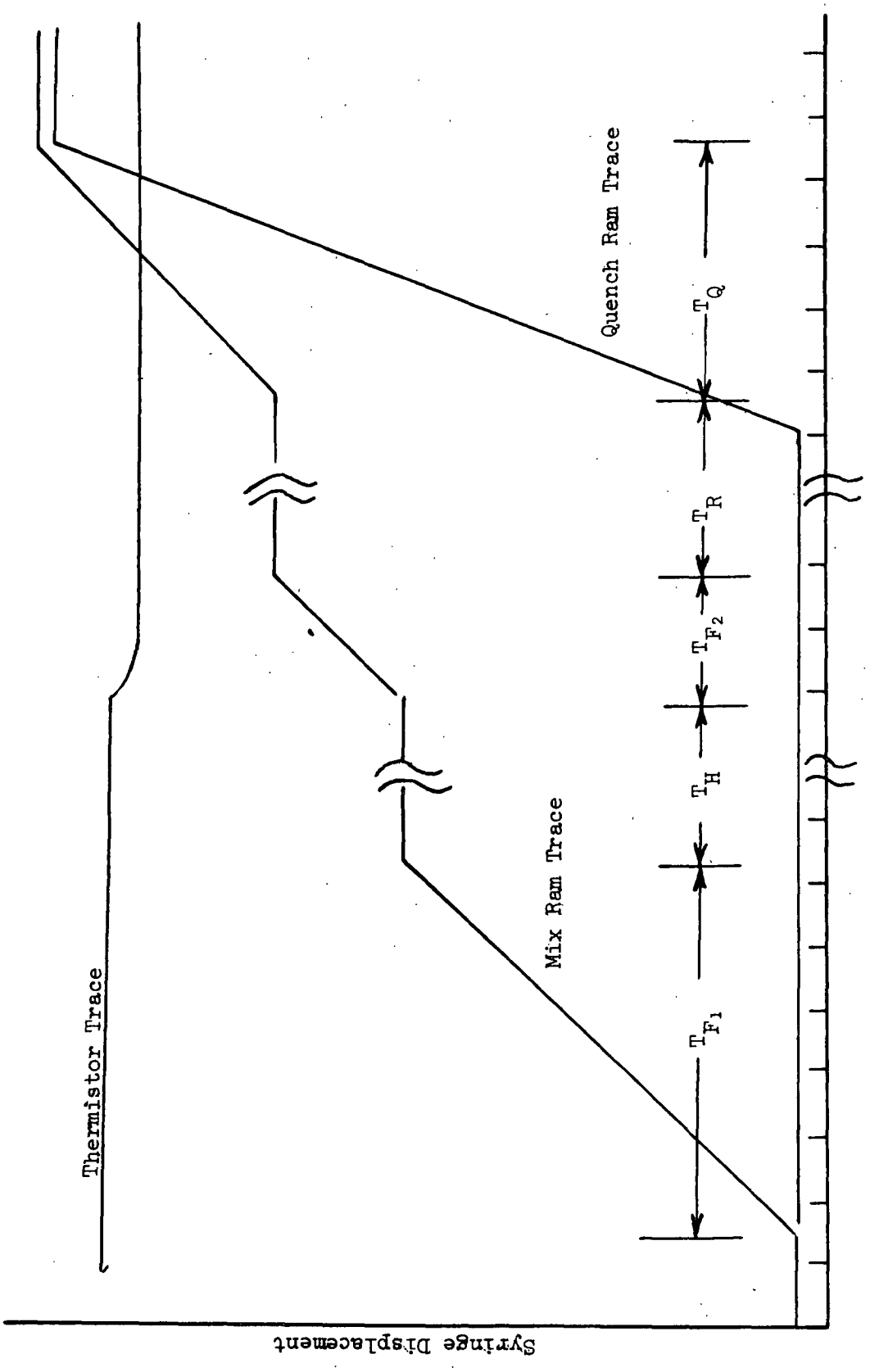


Figure 17. Photographic Recording of Syringe Movements

(F_1 and F_2 = Filling Sequences, H = Heating Period, R = Reaction Period, and Q = Quench Period)

introduce the cold liquid into the heated coils and determine the minimum time for thermal equilibration.

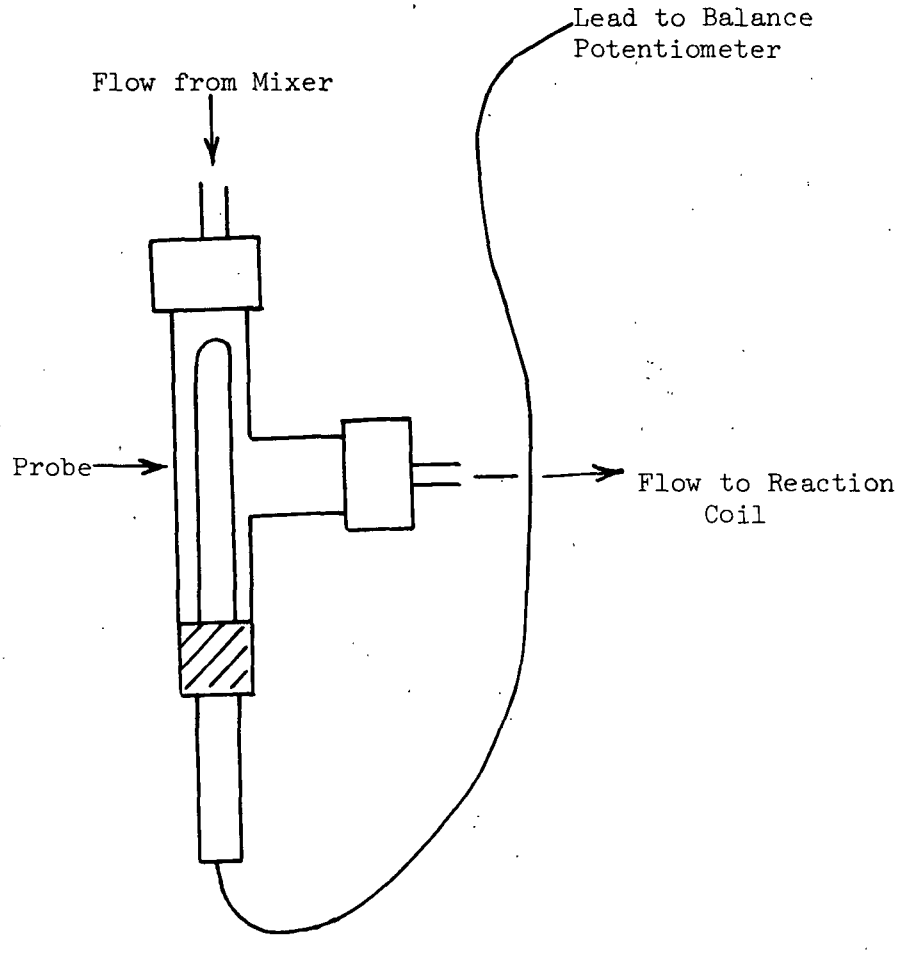


Figure 18. Thermistor Probe, Mounted in Swagelok Tee

The circuit for the thermistor is shown in Fig. 19; the details are as follows. "The sensing unit is a Conax TH-14-SS12-E-T3-MK125A-2.5" thermistor probe, which has a 1/8-inch diameter sheath of type 304 stainless steel. The thermistor forms one arm of an electrical bridge; the other arms and a mercury cell for bridge power are enclosed in a small metal box which can be placed close to the probe. A 10-foot shielded lead connects the bridge output to the oscillograph."

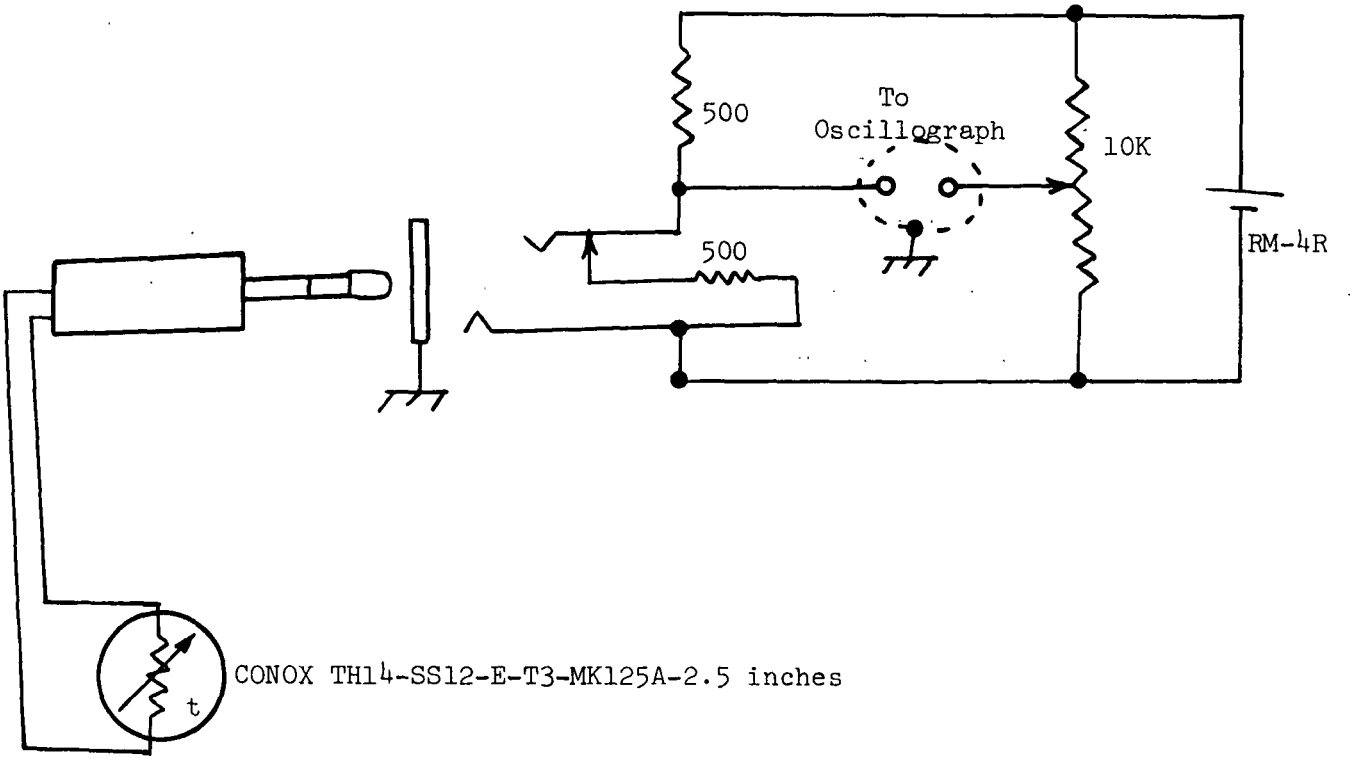


Figure 19. Thermistor Probe and Bridge

It has been found that the best way to adjust the balance potentiometer, for the thermistor at a given temperature, is to work at a gain of about 1/50 first. When the trace light is showing in the oscillograph window, the gain is turned up, and further adjustments made, until a gain of 1 is reached. The movement of the trace is so sensitive at the high gain that it is difficult to make preliminary adjustments; a lower gain is more suitable initially.

The response of the thermistor, for the introduction of water from a heating coil into the equilibrated thermistor tee, is about 2 seconds. This has been shown by a deflection of the trace on recorder paper. Thermocouples are more rapid in their response and may be used if the need arises.

ACKNOWLEDGMENTS

Acknowledgment is made to Larry Boggs for preparation of carbohydrate derivatives and performance of phenol-sulfuric acid analyses and for analyses by the phenol sulfuric acid method, and to Keith Hardacker for alteration of the flow reactor switchboard and installation of circuits for the thermistors.

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GLOSSARY OF TERMS USED

GMS — Glucosyl-metasaccharinic acid, the postulated alkali-stable acid formed by the stopping reaction from cellobiose.

PSA — The phenol-sulfuric acid method for determination of free sugars or glycosidic linkages.

Residual Absorbance — the color formed in the PSA method, for solutions of sugars after extended treatment with alkali, measured at 490 nm. The values are for 1 ml of solution, derived from 1 mg of cellobiose as starting material.

Residual Solutions — the alkaline solutions of cellobiose that have been heated until a constant residual absorbance has been obtained.

AQS — Anthraquinone sulfonic acid.

GLC — Gas-liquid chromatography — (often expressed as gas chromatography).